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- PATENT ABSTRACTS OF JAPAN vol. 4, no. 168  
(P-037), 20 November 1980 & JP 55 115163 A  
(SANKUSU K.K.), 4 September 1980,

## Description

[0001] The present invention relates to a fluorescent substance excellent in light emission a fluorescent composition such as, for example, an inking medium for use in an ink jet printer, containing the fluorescent substance and a fluorescent mark carrier such as, for example, postal envelopes, postal cards or postal parcels having a fluorescent mark formed by printing the fluorescent composition, and an optical reader.

[0002] In various fields of industries including the distribution industry, bar codes are widely utilized to control the physical distribution of commodities. The bar codes are also utilized having been printed on various cards such as, example, pre-paid cards, commutation cards and data cards. These bar codes are read by an optical reader such as, for example, an optical scanner which subsequently processes information represented by the bar codes. Most bar codes carried by surfaces of commodities or cards are in the form of a pattern of stripes printed by the use of a black inking medium against a white background and visible to human eyes under visible rays of light. This visible mark is printed directly on merchandise or printed on a shaped sheet-like carrier which is in turn affixed to merchandise.

[0003] On the other hand, attempts have been made to form a mark such as a bar code by the use of a fluorescent substance capable of emitting an infrared region of light so that the fluorescent mark can be identified by an optical reader. While the fluorescent mark is generally invisible to the human eyes, the fluorescent mark emits a fluorescent light when the fluorescent substance contained therein is excited upon irradiation of an external light of a particular wavelength and, therefore, by analyzing the fluorescent light with an optical reader, information represented by the fluorescent mark can be decoded or identified. Even the fluorescent mark is, as is the case with the visible mark, printed directly on merchandise or printed on a shaped sheet-like carrier which is in turn affixed to merchandise.

[0004] As compared with the system in which change in intensity of light reflected from the visible mark is read in handling merchandise, a system for handling merchandise, including an optical reader for reading the fluorescent mark, has numerous advantages, some of which are listed below.

(1) Reading of the fluorescent mark is seldom affected adversely by the color of the merchandise and, therefore, the reliability in reading the fluorescent mark is high with the reading error minimized.

(2) Even though the surface on which the fluorescent mark is formed becomes dirty, infrared rays of light emitted from the fluorescent mark has such a long wavelength that the reading error would seldom occur and the reliability is therefore high.

(3) Since the fluorescent substance is substantially colorless under visible rays of light, printing of the fluorescent mark on the merchandise will bring no adverse effect on the aesthetic appearance of the merchandise.

(4) Since the fluorescent substance is so invisible under visible rays of light that no one can recognize the presence of the fluorescent substance, it can provide security of information.

[0005] Particulars of interest in this connection are disclosed in, for example, the Japanese Patent Publications No. 55-33837, No. 60-29996 and No. 62-24024.

[0006] The fluorescent mark discussed above is formed by printing a fluorescent inking medium containing a fluorescent substance on a carrier such as, for example, a surface of the merchandise in a predetermined pattern. An infrared fluorescent inking medium has long been known and is disclosed in, for example, the United States Patent No. 4,202,491. The infrared fluorescent inking medium disclosed therein is prepared from an inorganic fluorescent substance containing one or a mixture of neodymium (Nd), ytterbium (Yb) and erbium (Er). The inorganic fluorescent substance which utilizes Nd as an optically active element is known to emit a fluorescent light having a maximum intensity at about 1,050 nm in wavelength when irradiated with an exciting light of 800 nm emitted by a GaAlAs light emitting diode. The inorganic fluorescent substance containing a mixture of Nb and Yb as an optically active element is known to emit a fluorescent light having a maximum intensity at about 980 nm in wavelength when irradiated with an exciting light of 800 nm emitted by a GaAlAs light emitting diode. Similarly, the inorganic fluorescent substance containing a mixture of Yb and Er as an optically active element is known to emit a fluorescent light having a maximum intensity at about 1,050 nm in wavelength when irradiated with an exciting light of 940 nm emitted by a GaAs light emitting diode, and the inorganic fluorescent substance containing a mixture of Nd, Yb and Er as an optically active element is known to emit a fluorescent light having a maximum intensity at about 1,050 nm in wavelength when irradiated with an exciting light of 800 nm emitted by a GaAlAs light emitting diode.

[0007] The fluorescent substance disclosed in, for example, the Japanese Patent Publication No. 56-4598 makes use as the optically active element of Nd having a high absorption characteristic with respect to the infrared region of light, in combination with a fluorescent material capable of exhibiting a high intensity of light emission such as, for example, an alkaline metal salt (for example,  $\text{Na}_2\text{MoO}_4$  or the like) which is material for the matrix having a high efficiency of transmission of exciting energies from the optically active element to the emission center, or Yb having an emission center capable of favorably matching in wavelength with a Si photodetector.

[0008] For example, the Japanese Patent Publications No. 54-22326 and No. 61-18231 disclose a method of de-

detecting the presence or absence of the fluorescent mark. In this known method, the fluorescent mark is prepared by the use of a fluorescent substance which emits a fluorescent light when irradiated with an exciting light within the infrared region of wavelength. This known method utilizes the difference between the center wavelength of the exciting light projected onto the fluorescent mark and that of the fluorescent light emitted from the fluorescent substance as a result of the irradiation of the exciting light and, for this purpose, only the fluorescent light is separated by an optical filter from rays of light reflected from the fluorescent mark so that the presence or absence of the fluorescent mark can be eventually detected.

[0009] The applicant has suggested a method of and an apparatus for detecting the position of a fluorescent mark by intermittently irradiating the fluorescent marking with the exciting light and then detecting the presence or absence of afterglow emitted from the fluorescent marking during the intermission of irradiation of the exciting light. (See, for example, the Japanese Laid-open Patent Publication No. 5-20512.)

[0010] Fig. 70 illustrates the prior art optical reading apparatus. The fluorescent mark shown therein is in the form of a fluorescent bar code 401 comprised of a pattern of parallel bars formed by printing the fluorescent inking medium on a sheet-like carrier 404 such as, for example, a label. The fluorescent inking medium used to form the bar code 401 contains fluorescent microparticles dispersed and retained in a binder, said fluorescent microparticles being of a kind which emit, when excited by an exciting light of a particular wavelength, for example, infrared rays of light 402, a fluorescent light 403 of a wavelength different from that of the infrared rays of light 402.

[0011] An optical reading apparatus for reading information from the fluorescent bar code 401 includes a light emitter 405 for emitting the infrared rays of light 402, a light receiver 407 for detecting the fluorescent light 403 from the bar code 401 and rays of light 406 reflected from the carrier 404 and for converting them into an electric signal, an amplifier 408 for amplifying the electric signal and for outputting an analog reproduction signal, and a signal detector 409 for detecting from the analog reproduction signal of the amplifier 408 information represented by the bar code 401. The signal detector 409 used therein includes an analog-to-digital (A/D) converter which is operable to digitize the analog reproduction signal so that the information represented by the fluorescent bar code 401 can be reproduced.

[0012] For digitization of the analog reproduction signal, a comparator is generally utilized, having an input stage which is adapted to receive the analog reproduction signal A and a slice signal B of a predetermined level shown in Fig. 66 so that the analog reproduction signal A can be sliced by the slice signal B to provide a digitized signal.

(Problem 1)

[0013] In the various fluorescent substances and the various fluorescent marks formed by printing the fluorescent inking media containing the respective fluorescent substances, both having hitherto been suggested, neither the relationship between the particle size of the particular fluorescent substance and the wavelength of the exciting light used nor the relationship between the particle size of the particular fluorescent substance and the wavelength of the fluorescent light emitted by such particular fluorescent substance has been taken into consideration. The conventional fluorescent substance has a particle size as relatively large as 5 to 6  $\mu\text{m}$ . On the other hand, for a light source for exciting the fluorescent substance, a semiconductor laser, for example, is generally utilized, capable of emitting a laser beam of about 0.8  $\mu\text{m}$  in wavelength while the fluorescent light emitted from the conventional fluorescent substance has a wavelength of about 1  $\mu\text{m}$ .

[0014] As discussed above, the conventional fluorescent particles have a relatively great particle size, i.e., a particle size as great as about 5 to 7.5 times the wavelength of any one of the exciting light and the fluorescent light. For this reason, if the fluorescent mark is prepared by the use of the fluorescent inking medium containing the fluorescent particles of that particle size, the fluorescent particles are deposited in such an overlapping relation that the exciting light projected towards a deposit of the fluorescent inking medium will not reach some of the fluorescent particles at a deep region of the deposit of the fluorescent inking medium, and for this reason, the efficiency of activation (excitation) of the fluorescent substance is lowered.

[0015] Even if some of the fluorescent particles at the deep region of the deposit of the fluorescent inking medium are excited to emit a fluorescent light, the fluorescent light so emitted tends to be partly intercepted by other fluorescent particles residing over such some of the fluorescent particles within the deposit of the inking medium, with the intensity of the fluorescent light consequently lowered. Consequently, the fluorescent light of such a low intensity often creates a problem associated with the reliability in detecting the presence or absence of the fluorescent mark.

[0016] Thus, partly because the efficiency of activation (excitation) of the fluorescent substance is low and partly because part of the fluorescent light excited will not emerges outwardly from an exterior surface of the deposit of the fluorescent inking medium and, hence, the intensity of the fluorescent light is consequently low, the prior art fluorescent substance poses a problem associated with the reliability in detecting the presence or absence of the fluorescent mark.

**(Problem 2)**

[0017] The fluorescent substance generally has such a property that when irradiated with the exciting light the fluorescent substance is activated to emit a fluorescent light in a progressively increasing quantity, but in the absence of the exciting light the quantity of the fluorescent light emitted decreases progressively. With the conventional fluorescent substance, the length of time, that is, the rise time, which passes from the start of irradiation of the exciting light upon the fluorescent substance and until the resultant fluorescent light attains a desired intensity is long. For this reason, a high velocity of movement of the fluorescent mark carrier relative to the optical reader cannot be employed, constituting an obstruction to the use of a high speed optical reader. If the relative velocity is increased, information represented by the fluorescent mark will no longer be read accurately and properly.

[0018] Although this is related to the relatively long rise time of the fluorescent light referred to above, the conventional fluorescent substance has a length of time (that is, the fall time) which passes from the interruption of irradiation of the exciting light upon the fluorescent substance and until the intensity of the fluorescent afterglow attains zero, that is, until the fluorescent light is no longer detected is long as well. For this reason, where the fluorescent mark consists of a plurality of parallel fluorescent bars, reduction in spacing between each neighboring fluorescent bars will render the light receiving element to detect a fluorescent afterglow emanating from the adjoining fluorescent bar, failing to provide an accurate information reading.

**(Problem 3)**

[0019] Inorganic powdery fluorescent pigments such as Nd, Yb and Er discussed hereinbefore have a relatively large particle size. Although this particle size would pose no problem if the fluorescent particles are tramped down with resin before use, the use of the fluorescent pigment of a relatively large particle size in an inking medium for use with an ink jet printer would, unless the particle size is reduced, result neither in a homogenous and beautiful print, nor in a high resolution during information reading. On the other hand, if the fluorescent particles are finely pulverized with the use of a mill, the fluorescent output would eventually decrease considerably.

[0020] The inventors of the present invention have also found that, in addition to the above discussed problems, the inorganic fluorescent pigments bring about an additional problem in that the response of the fluorescent substance to emit the fluorescent light subsequent to receipt of the exciting light is so low that a high speed reading is difficult to achieve.

**(Problem 4)**

[0021] In the Japanese Patent Publication No. 56-4598 referred to above, there is disclosed that the matrix material of the infrared-excitable fluorescent substance contains alkaline metal cations,  $\text{Li}^+\text{Na}^+$ , if an anion thereof is chosen  $\text{MoO}_4^{2-}$  or  $\text{W}_4^{2-}$ . Since a salt of alkaline metal which is generally a monovalent metal has a relatively weak bond between the anion and the cation because of a small valence sufficient to be easily released to form a hydrate, the alkaline metal salt is water-soluble. Accordingly, the fluorescent substance prepared from the alkaline metal salt as a matrix material is extremely poor in water resistance to such an extent as to result in an obnoxious problem in practical use.

[0022] The infrared-excitable fluorescent substance is prepared by weighing, mixing and pressure-forming only the starting materials (for example,  $\text{Na}_2\text{CO}_3$ ,  $\text{MoO}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$ ), incinerating the preformed mixture and subsequently mechanically pulverizing it to provide the powdery fluorescent substance. In such case, the resultant fluorescent particles have a minimum particle size as small as about  $5\text{ }\mu\text{m}$ . Although this particle size permits the fluorescent particles to be used as a material for a printing ink medium such as used in, for example, a screen printing technique, the fluorescent particles of this particle size cannot be used as a material for an inking medium for use with an ink jet printer or for use in an inked ribbon. This is because the inking medium for use in the practice of a printing technique requires the fluorescent substance of  $1\text{ }\mu\text{m}$  or smaller in particle size, the fluorescent substance of about  $5\text{ }\mu\text{m}$  in particle size is not suited as a material for the inking medium that is used with the ink jet printer or in the inked ribbon.

[0023] The Japanese Laid-open Patent Publication No. 5-261634 referred to above discloses that the fluorescent substance having its matrix material in the form of a salt of  $\text{PO}_4$  and activated by Nd and Yb can be used in an inking medium for use in an offset printing technique provided that such fluorescent substance is pulverized to a particle size within the range of  $0.1$  to  $3\text{ }\mu\text{m}$ .

[0024] However, the infrared-excitable fluorescent substance of this system has been found that both of the rise time, required for it to emit a fluorescent light of the maximum intensity subsequent to irradiation of infrared rays of light, and the fall time required for the intensity of the fluorescent light to attain zero subsequent to interruption of the infrared irradiation are extremely long, and therefore, it cannot satisfactorily be used where the exciting light is in the form of a pulsating light of short duration and/or where a high speed reading with, for example, a high speed scanner

is desired.

[0025] The inventors of the present invention, in an attempt to develop an infrared-excitabile fluorescent substance having a high response, have examined the use of  $\text{Na}_2\text{MoO}_4$  as a matrix of the infrared-excitabile fluorescent substance, but have found that, because  $\text{Na}_2\text{MoO}_4$  is water-soluble, the fluorescent substance having its matrix added with optically active elements has exhibited a poor water resistance. Also, the fluorescent substance obtained had a particle size greater than a few microns and have therefore been found not suited for use as a material for the ink jet printer or the inked ribbon or in a printing technique such as an offset printing process.

#### (Problem 5)

[0026] Hitherto, in preparing a fluorescent composition such as, for example, the inking medium for use with an ink jet printer and containing fluorescent particles, none of the particle size of the fluorescent substance used, the density of the fluorescent substance and/or the density of a binder used, and the relationship among viscosity, surface tension, specific resistance and pH value has not taken into consideration. For this reason, the fluorescent particles contained in the fluorescent composition have such problems that the fluorescent particles are apt to sediment in the fluorescent composition, exhibiting an unsatisfactory dispersion stability, that the fluorescent composition tends to run during the printing and/or that the fluorescent output is low.

#### (Problem 6)

[0027] In the prior art fluorescent inking medium containing the fluorescent particles, the fluorescent substance is employed in a quantity generally within the range of 30 to 85 wt% relative to the total weight of the inking medium and is in the form of an inorganic compound having a relatively large particle size as discussed hereinabove. The use of the fluorescent substance in such a large quantity brings about such a problem that a fluorescent ink deposit formed by printing the fluorescent inking medium is so raised as to provide a visible indication of the presence of the ink deposit. This is problematic in terms of security particularly when a fluorescent mark is desired to be formed by depositing the inking medium at a location where the ink deposit will not constitute any obstruction to the eyes.

#### (Problem 7)

[0028] With respect to the fluorescent ink deposit formed by the use of the conventional fluorescent inking medium containing the fluorescent particles, no surface roughness of the ink deposit has been studied. Since the fluorescent substance of the relatively large particle size as discussed above has been employed, the surface of the ink deposit is relatively rough, having minute surface irregularities. Irradiation of the exciting light upon the rough-surfaced ink deposit tends to result in scattering of the exciting light upon the surface of the ink deposit, accompanying reduction in quantity of the exciting light penetrating into the fluorescent ink deposit. Also, with the rough-surfaced ink deposit, the fluorescent light emitted internally from the fluorescent ink deposit is apt to scatter in all directions at the surface of the ink deposit and, therefore, the quantity of the fluorescent light received by a light receiving element may be reduced correspondingly.

[0029] Once the above discussed phenomenon occurs, an output generated from the light receiving element in response to detection of the fluorescent light emitted from the fluorescent ink deposit is so low as to bring about a problem associated with the reliability in detecting the presence or absence of the fluorescent mark.

[0030] An optical reading apparatus used in connection with the fluorescent mark is known and includes a semi-transparent mirror disposed generally intermediate between the fluorescent mark to be detected and a photoelectric detector assembly inclusive of light emitting and receiving elements. The known optical reading apparatus is so structured that the exciting light emitted from the light emitting element may be projected through the semitransparent mirror onto the fluorescent mark carrier so that the fluorescent light emitted from the fluorescent mark on the carrier can pass through the same semitransparent mirror before it is detected by the light receiving element. With this structure, it has been observed that as the exciting light travels through the semitransparent mirror, generally half of the exciting light may be reflected in directions other than the direction towards the fluorescent mark carrier and/or that as the fluorescent light emitted from the fluorescent mark on the carrier travels through the semitransparent mirror, generally half of the fluorescent light may be reflected in directions other than the direction towards the light receiving element. For this reason, the quantity of the exciting light necessary to activate the fluorescent substance is in practice small and, hence, the quantity of the fluorescent light emitted is correspondingly small and, yet, the light receiving element receives the fluorescent light in a quantity generally half of the actually emitted fluorescent light. Therefore, the light receiving element issues a considerably low output, so low as to bring about a problem associated with the reliability in detecting the fluorescent mark.

[0031] In the prior art optical reading apparatus, the exciting light emitted from the light emitting element forms a

round irradiating pattern of a size sufficient to encompass the size of the bar code forming the fluorescent mark. Irradiation of the round light spot upon the fluorescent mark does not afford a sufficient area of surface to be illuminated and the intensity of the fluorescent light emitted from the fluorescent mark is consequently low. If an attempt is made to increase the size of the round light spot to thereby increase the area of surface to be illuminated, the exciting light will encompass not only the bar code of interest, but also the bar code adjoining such bar code of interest. This in turn brings about reduction in S/N (signal-to-noise) ratio, accompanying a problem associated with the reliability in detecting the fluorescent mark.

**[0032]** In designing the prior art optical reading apparatus, neither the rise time of the fluorescent light subsequent to irradiation of the exciting light, nor the relationship between the width of a slit extending in a direction of transport of the fluorescent mark carrier and the speed of transport of the fluorescent mark carrier is taken into consideration.

**[0033]** Also, neither the fall time of the fluorescent lights subsequent to interruption of the exciting light, nor the relationship between the interval between the neighboring bars of the fluorescent mark (i.e., the fluorescent bar code) and the speed of transport of the fluorescent mark carrier is taken into consideration.

**[0034]** Because of the foregoing, no information represented by the fluorescent ink deposit on the fluorescent mark carrier can be read.

**[0035]** In the prior art optical reading apparatus, a slit member is interposed between the sheet-like fluorescent mark carrier such as, for example, a paper, and an object lens assembly so that only that portion of the fluorescent light emitted from the fluorescent mark which is desired to be detected is received by the light receiving element through the slit in the slit member. Although this will bring about no problem if the fluorescent mark carrier has a substantially uniform thickness, there is a problem in that, if the fluorescent mark carrier having a relatively great, but irregular thickness is transported, the fluorescent mark carrier being transported may be blocked with its front engaged with the slit and/or the slit will be damaged.

**[0036]** The prior art method of detecting the mark such as disclosed in the Japanese Patent Publications No. 54-22326 and No. 61-18231 and the Japanese Laid-open Patent Publications No. 3-16369 and No. 5-20512 all referred to above, is such that the fluorescent light emitted from the fluorescent mark as a result of excitation by the exciting light is detected by a detector. However, the quantity of the fluorescent light incident on the detector considerably varied with change in environments and conditions in and under which the detection is performed and, therefore, in order to secure a high accuracy of detection, a complicated circuit processing is required, or the condition of use is limited.

**[0037]** As a result of studies conducted by the inventors of the present invention in view of the foregoing problems, it has been found that any one of the prior art detecting method is unable to properly and accurately monitor the change in detecting condition because of an insufficient quantity of information available other than data associated with the fluorescent mark.

**[0038]** In another prior art method in which an optical filter used to separate the exciting light, which has been reflected, and the fluorescent light from each other, since the wavelength of the emission center of the reflected exciting light and that of the fluorescent light are close to each other and the intensity of the fluorescent light is extremely low as compared with that of the reflected exciting light, the both cannot be properly separated from each other with no difficulty and, in a certain case, most of the reflected exciting light may remain unseparated and enter the light receiving element together with the fluorescent light. Once this occurs, the accuracy of detection is lowered.

**[0039]** According to the fluorescent mark detecting method disclosed in, for example, the Japanese Laid-open Patent Publications No. 3-16369 and No. 5-20512 referred to above, if external rays of light of a wavelength matching with or in the vicinity of the wavelength of the fluorescent light exist in the environment in which the fluorescent light is being detected, such rays of light may be sensed by and converted into an electric output by the light receiving element. This leads to generation of false information that, even though no fluorescent light has yet been emitted, the fluorescent light was detected. In order to avoid such false information, both of the site of emission of the exciting light and the site of detection of the fluorescent light are required to be shielded from the external light, thus limiting the environment in which the system is used.

**[0040]** In the optical reading apparatus of a structure shown in Fig. 71, both of the level and the amplitude of the analog reproduction signal discussed hereinbefore are considerably affected by physical surface properties of the carrier on which the bar code is formed in the form of the fluorescent mark. More specifically, where the surface of the carrier is made of material having a propensity of absorbing a transparent inking medium and also the exciting light projected from an illuminator unit, the quantity of the fluorescent light emitted from the fluorescent bar code and the quantity of light reflected from the carrier are so small that, as shown in Fig. 71(b), the analog reproduction signal exhibits a low level and a low amplitude.

**[0041]** Also, where the carrier is made of material having a propensity of absorbing the transparent inking medium and also that of reflecting the light projected by the illuminator unit, the analog reproduction signal is apt to offset towards a high level as shown in Fig. 71(c). Moreover, where the carrier is made of material having a propensity of absorbing little transparent inking medium, but absorbing the light projected by the illuminator unit, the analog reproduction signal exhibits an increased amplitude as shown in Fig. 71(a).

[0042] Accordingly, with the prior art reading apparatus in which variation in waveform of the analog reproduction signal resulting from difference in type of the carriers on which the fluorescent bar codes are formed is taken into consideration, when the single reading apparatus is used to read one at a time the fluorescent bar codes formed on, for example, the respective carriers made of different materials, or when the reading apparatus is used to read one at a time the fluorescent bar codes formed on different portions of the single carrier which are made of varying materials, a problem is apt to occur in that the bar codes will not be accurately read. This problem may be avoided if an optical filter (a single wavelength filter) operable to cut off the entire light reflected from the carrier is disposed in front of the light receiving element. However, the single wavelength filter is expensive and cannot, in terms of cost, be installed in the optical reading apparatus and, instead, the above discussed problem does often occur since a band-pass filter operable to cut off a portion of the reflected light is generally employed.

[0043] Accordingly, a primary object of the present invention is to provide a highly reliable fluorescent substance having a high emissive output, a fluorescent composition and a fluorescent mark carrier, system all of which are effective to substantially eliminate the above discussed problems inherent in the prior art.

[0044] Another important object of the present invention is to provide the fluorescent substance and the fluorescent composition which are effective to substantially eliminate the above discussed problems inherent in the prior art, excellent in durability, fine in particle size suitable for use in various printing techniques such as those employing an ink jet printer or an inked ribbon, and capable of exhibiting a high response.

[0045] A further important object of the present invention is to provide an optically detectable mark effective to substantially eliminate the above discussed problems inherent in the prior art and with which change in environmental conditions in which data are being detected can be readily and properly determined.

[0046] The invention in its first embodiment is directed to the fluorescent substance of a kind capable of emitting, in response to irradiation of the exciting light, a fluorescent light of a wavelength different from that of the exciting light and is characterized in that, in order to accomplish the foregoing objects, the average particle size of the fluorescent substance being of super microparticles is smaller than the maximum intensity of the fluorescent light emitted by such fluorescent substance.

[0047] The invention in its second embodiment is directed to the fluorescent substance of a kind capable of emitting, in response to irradiation of the exciting light, a fluorescent light of a wavelength different from that of the exciting light and is characterized in that, in order to accomplish the foregoing objects, the average particle size of the fluorescent substance being of ultra-microparticles is smaller than the maximum intensity of the exciting light.

[0048] The fluorescent composition according to the third embodiment of the invention is characterized in that, it comprises a fluorescent substance in the form of ultra-microparticles capable of emitting a fluorescent light of a wavelength different from that of the exciting light and having an average particle size smaller than the wavelength of the maximum intensity of the fluorescent light, a binder transparent to both of the exciting light and the fluorescent light, and a solvent.

[0049] The fluorescent composition according to the forth embodiment of the invention is characterized in that, it comprises a fluorescent substance in the form of ultra-microparticles capable of emitting a fluorescent light of a wavelength different from that of the exciting light and having an average particle size smaller than the wavelength of the maximum intensity of the exciting light, a binder transparent to both of the exciting light and the fluorescent light, and a solvent.

[0050] The fluorescent mark carrier according to the fifth embodiment of the invention is characterized in that, the fluorescent mark containing the fluorescent substance in the form of ultra-microparticles capable of emitting a fluorescent light of a wavelength different from that of the exciting light and having an average particle size smaller than the wavelength of the maximum intensity of the fluorescent light is printed thereon.

[0051] The fluorescent mark carrier according to the sixth embodiment of the invention is characterized in that, the fluorescent mark containing the fluorescent substance in the form of ultra-microparticles capable of emitting a fluorescent light of a wavelength different from that of the exciting light and having an average particle size smaller than the wavelength of the maximum intensity of the exciting light is printed thereon.

[0052] According to the first, third and fifth embodiment of the invention described above, since the fluorescent substance is in the form of ultra-microparticles having an average particle size smaller than the wavelength of the fluorescent light of a maximum intensity emitted from the fluorescent substance and, in other words, since the wavelength of the fluorescent light is greater than the particle size of the fluorescent particles, the fluorescent light emitted from the fluorescent particles arrives at a surface of the fluorescent ink deposit having passed through the fluorescent particles positioned thereabove. Accordingly, the fluorescent light can be effectively radiated, detection of the fluorescent light is ensured, and the reliability can be increased. embodiment of the

[0053] According to the second, fourth and sixth embodiment of the invention described above, since the fluorescent substance is in the form of ultra-microparticles having an average particle size smaller than the wavelength of the exciting light of a maximum intensity emitted from the fluorescent substance and, in other words, since the wavelength of the exciting light is greater than the particle size of the fluorescent particles, the exciting light can effectively irradiate



the fluorescent particles in a lower region even though the fluorescent particles in an upper region exist above the lower region. Therefore, the efficiency of activation (excitation efficiency) of the fluorescent substance is high and, consequently, detection of the fluorescent light is ensured accompanied by an increase in reliability.

[0054] The fluorescent substance may be obtained in that the flux material containing the salt expressed by  $T_2RO_4 \cdot nH_2O$  is added with at least one optical active element selected from the group consisting of Nd and Yb, at least one oxide of one of Mo and W and an alkaline earth metal and is then calcinated, followed by dissolution of the flux material with a solvent to remove it.

[0055] With respect to the particle size of the fluorescent substance so prepared by the calcination referred to above, comparison of the prior art powdery fluorescent substance having a matrix comprised of  $Na_2MoO_4$  and mechanically pulverized after the calcination, the powdery fluorescent substance of the present invention having a matrix of  $CaMoO_4$  and mechanically pulverized after the calcination and the fluorescent substance added with a water-soluble flux material during the calcination, but with the flux material having been removed by flushing subsequent to the calcination, have shown that, while the prior art substance was of a particle size of about  $5\mu m$  at minimum, the substance of the present invention was found to be microparticles in which primary particles of a particle size within the range of about 2 to  $5\mu m$  were secondarily aggregated, and the substance introduced with the flux material was found to be microparticles of a particle size not greater than  $1\mu m$ .

[0056] In the solid phase reaction induced by the calcination the particle size of the starting material is one of factors that determine the particle size of a reaction product (in this case, the fluorescent substance). The smaller the particle size of the raw material, the smaller the particle size of the reaction product. Accordingly, the material of a particle size as small as possible should be chosen for the raw material.

[0057] Another one of the factors that determine the particle size of the fluorescent substance is the surface area of contact among the raw materials that induce the solid phase reaction. The larger the contact surface area, the more often the solid phase reaction occurs, resulting in acceleration of the particle growth. By way of example, considering the reaction of only the matrix comprised of  $CaMoO_4$  employed in the present invention, the solid phase reaction may be expressed by  $[CaCO_3(s) + MoO_3(s) \rightarrow CaMoO_4(s) + CO_2(g)]$ . (In this case, the calcinating temperature is  $750^\circ C$  which is lower than the decomposition temperature,  $900^\circ C$ , of  $CaCO_3$ , but it is suspected that such a reaction,  $[CaCO_3(s) \rightarrow CaO(s) + CO_2(g)]$ , may occur as a result of somewhat decomposition.)

[0058] If for the flux material  $Na_2MoO_4$  is employed which has a melting point at  $687^\circ C$  which is lower than the calcination temperature of  $750^\circ C$ , the solid phase reaction takes place.  $CaCO_3$  and  $MoO_3$  are dispersed in the flux melt, accompanied by reduction in surface contact area among the raw materials. In view of this, the particle growth appears to be disturbed, resulting in reduction in particle size of the reaction product.

[0059] With respect to the light emission intensity, so long as the fluorescent substance added with and activated by, for example Nd and Yb is concerned, when emission outputs exhibited respectively by the conventional fluorescent substance containing  $Na_2MoO_4$  as a matrix, the fluorescent substance of the present invention containing  $CaMoO_4$  as a matrix and the fluorescent substance having a particle size not greater than  $1\mu m$ , as a result of excitation by the pulsating exciting light are compared, the fluorescent substance of the present invention has resulted in reduction of the light emission intensity down to about 80% of that exhibited by the conventional fluorescent substance and the fluorescent substance of the particle size not greater than  $1\mu m$  has resulted in reduction of the light emission intensity down to about 40% of that exhibited by the conventional fluorescent substance.

[0060] However, when the sensitivity of an Si photodetector is taken into consideration, these emission intensities would bring about no problem in practice. This is because this reduction in emission intensity discussed above is attributable to the particle size of the fluorescent substance being smaller than that of the conventional fluorescent substance and not attributable to the type of matrix material.

[0061] The emission intensity and the response are associated with the transition probability of the rare earth element. Specifically, the higher the transition probability, the higher emission intensity and the higher the response. The optical transition of Nd and Yd which are used in the practice of the present invention as an optical active element is a transition of f-electrons between energy levels and is known as a forbidden transition in terms of the parity of the wave function.

[0062] However, in crystals, levels having a parity reverse to the f-trajectory due to the crystal field are mixed up and the f-f transition is permitted to a certain extent. This tolerance is large if the symmetric property of the crystal field is low and, hence, the transition probability is high. By way of example, while  $Na_2MoO_4$  employed in the conventional fluorescent substance is of a cubic system,  $CaMoO_4$  employed in the practice of the present invention is of a pyramidal quadratic system and, therefore, the symmetric property of the crystal is low. Accordingly, in terms of material, the fluorescent substance of the present invention cannot be considered inferior to the conventional fluorescent substance in respect of the emission intensity and the response.

[0063] Also, the response does not depend on the particle size, and the fluorescent substance of the present invention which is considered having a high transition probability exhibits a somewhat higher response.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0064]

Fig. 1 is a diagram showing an emission spectrum exhibited by a complex salt of cinnamic acid with neodymium and ytterbium (1/1) according to an embodiment of the present invention;

Fig. 2 is a characteristic graph showing the relationship between the molar ratio of Nd/Yb contained in the complex salt of cinnamic acid with neodymium and ytterbium (1/1) and the emission intensity;

Fig. 3 is characteristic graphs showing the irradiation timing of an exciting light and respective conditions of emission of florescent light from two types of fluorescent substances;

Fig. 4 is a schematic diagram showing the relationship among the slit length in a slit member, the velocity of transport of a fluorescent mark carrier and the intervals of fluorescent ink deposits on the carrier;

Fig. 5 is a graph showing the relationship among the viscosity of an inking medium of the present invention for use with an ink jet printer according to the present invention, a relative output and the degree of variability of the size of a droplet of the inking medium;

Fig. 6 is a graph showing the relationship among the surface tension of the inking medium of the present invention for use with the ink jet printer and the degree of variability of the size of the ink droplet;

Fig. 7 is a graph showing the relationship between the specific resistance of the ink droplet and the degree of variability of the ink droplet;

Fig. 8 is a graph showing the relationship between the pH value of the inking medium of the present invention for use with the ink jet printer and the dispersion stability;

Fig. 9 is a plan view of a postal envelope formed with a fluorescent mark according to an embodiment of the present invention;

Fig. 10 is a plan view showing another example of the postal envelope formed with the fluorescent mark according to the embodiment of the present invention;

Fig. 11 is a flowchart showing the manner in which a bar code information is applied to postal matter and the bar code so applied is read out.

## BEST MODES FOR CARRYING OUT THE INVENTION

[0065] For the purpose of easy understanding of the present invention, the present invention will be described under the following headings:

## 1. Fluorescent Substance and Fluorescent Composition

## 1. [Fluorescent Substance and Fluorescent Composition]

Fluorescent Composition 1

[0066] The fluorescent substance of the present invention is an organic metallic compound containing, as an optical active element, at least neodymium (Nd), or preferably an organic metallic compound containing, as an optical active element, a mixture of Nd and ytterbium (Yb). An organic material of this organic metallic compound is at least one organic material selected from the group consisting of carboxylic acid, ketone, ether and amine.

[0067] More specifically, the organic metallic compound referred to above may be at least one organic metallic compound selected from the group consisting of neodymium cinnamate, a complex salt of cinnamic acid with neodymium and ytterbium, a complex salt of benzoic acid with neodymium and ytterbium, neodymium naphthoate and a complex salt of naphthoic acid with neodymium and ytterbium. Of them, a complex salt of carboxylic acid comprising a cinnamic acid and Nd and Yb is preferred.

[0068] The molar ratio of Nd relative to Yb (Nd:Yb) is preferably selected within the range of 9.5:5 to 3:7 and more preferably within the range of 9:1 to 5:5, by the reason which will become clear from the subsequent description made with reference to Fig. 2.

[0069] This fluorescent substance may be synthesized in any suitable manner, but the use of an ion-exchange reaction in an aqueous solution, such as published by M.D. Taylor, et al., in J. Inorg. Nucl. Chem., 30, 1530-1511 (1968), or an elimination reaction of isopropoxide in a non-polarity solvent such as published by P.N. Kapoor, et al., in Synth. React. Inorg. Met. -Org. Chem., Vol. 17, 507-523 (1987), is preferred for synthesization of the fluorescent substance.

[0070] Unlike an inorganic fluorescent substance, this organic fluorescent substance contains in its molecules an organic material such as carboxylic acid,  $\beta$ -diketone, cyclic ether or cyclic amine, and in particular, cinnamic acid which is one kind of the carboxylic acids is preferred because it has an excellent chemical stability and gives rise to a relatively high emission output.

[0071] This fluorescent substance has an average primary particle size not greater than about 80% of the wavelength (810 nm) of the infrared rays, that are used as exciting light, at the maximum intensity thereof and not greater than about 70% of the wavelength (980 nm) of the fluorescent light, emitted from such fluorescent light, at the maximum intensity thereof. Since this fluorescent substance does not form a block of primary particles such as observed in the inorganic fluorescent substance and will not damage crystals thereof, it can easily be pulverized and will become finer when dispersed in a binder. Therefore, when an inking medium for use with the ink jet printer is to be prepared using this organic fluorescent substance, the latter is satisfactorily stabilized having been dispersed in the binder with no substantial possibility of being precipitated and, therefore, the use of such inking medium will not result in a nozzle clogging or an insufficient jetting of droplets of the inking medium.

[0072] A specific methods of making the fluorescent substance will now be described.

[0073] 1.24 g (8.37 mol) of cinnamic acid and 0.37 g (8.37 mol) of sodium hydroxide are added to 120 ml of ion-exchange water while being stirred, to provide an aqueous solution of sodium cinnamate. The pH value of this aqueous solution is adjusted to 10 by the use of an aqueous solution of 0.1N sodium hydroxide.

[0074] Separately therefrom, 0.54 g (1.39 mol) of neodymium chloride hexahydrate and 0.54 g (1.39 mol) of ytterbium chloride hexahydrate are dissolved completely in 50 ml of ion-exchange water to provide an aqueous solution which is subsequently added, while being stirred, to the aqueous solution of sodium hydroxide. This addition results in formation of sediment.

[0075] Thereafter, the Ph value of the reaction liquid is adjusted to 5 by the addition of 0.1N hydrochloric acid and is stirred for two hours, followed by filtration of the sediment to obtain a filtrate. The filtrate is, after having been washed, dried at 120°C for 5 hours to provide 1.62 g of a complex salt of cinnamic acid with neodymium and ytterbium (1/1). This quantity of the resultant fluorescent substance corresponds to the yield of 93.1%.

[0076] Fig. 1 illustrates an emission spectrum exhibited by the complex salt of cinnamic acid with neodymium and ytterbium (1/1) when the latter is excited by exciting light emitted from a GaAlAs light emitting diode used as a source of excitation, showing the maximum peak wavelength appearing at about 980 nm.

[0077] Fig. 2 illustrates a characteristic graph showing the relationship between the molar ratio of Nd relative to Yb (Nd/Yb) and the emission intensity. As shown therein, a high emission output is exhibited when the Nd/Yb molar ratio is within the range of 9.5/5 to 3/7 and preferably within the range of 9/1 to 5/5.

[0078] The complex salt of cinnamic acid with neodymium and ytterbium (1/1) has an average particle size of 0.2  $\mu\text{m}$  which corresponds to about 25% of the wavelength (0.81  $\mu\text{m}$ ) of the maximum intensity of the exciting light and about 20% of the wavelength (0.98  $\mu\text{m}$ ) of the maximum intensity of the fluorescent light emitted by the complex salt of cinnamic acid with neodymium and ytterbium (1/1) and which is thus extremely smaller than the wavelength of the maximum intensity of any one of the exciting light and the fluorescent light.

[0079] The above discussed method may be equally employed to prepare a complex salt of benzoic acid with neodymium and ytterbium and this can be accomplished if cinnamic acid used in the practice of the above discussed method is replaced with benzoic acid. Even the resultant fluorescent substance, that is, complex salt of benzoic acid with neodymium and ytterbium, has an average particle size which is extremely smaller than the wavelength of the maximum intensity of any one of the exciting light and the fluorescent light.

[0080] The fluorescent substance in the form of super microparticles of an organic metallic compound such as, for example, neodymium cinnamate, neodymium naphthoate, complex salt of naphthoeic acid with neodymium and ytterbium or neodymium benzoate may be equally employed.

[0081] Since the wavelength of the maximum intensity of the exciting light used to excite any of those fluorescent substances and the wavelength of the maximum intensity of the fluorescent light emitted therefrom exceed about 0.8  $\mu\text{m}$  (800 nm), the use of the fluorescent substance having an average particle size not greater than 0.8  $\mu\text{m}$  results in an effective entry of the exciting light and an effective emission of the fluorescent light.

[0082] Fig. 3 illustrates characteristic graphs showing a condition of the exciting light being irradiated and a condition of the fluorescent light emitted from the fluorescent substance. Fig. 3(a) illustrates the condition of irradiation from the GaAlAs light emitting diode and the exciting light emitted therefrom is generally in the form of a train of pulses having a pulse repetition period of 2,000  $\mu\text{sec}$ .

[0083] Fig. 3(b) illustrates the condition of emission of the fluorescent light from the complex salt of cinnamic acid with neodymium and ytterbium (1/1), prepared by the previously discussed method, showing that the rise time  $t_r$  required for the intensity of the fluorescent light emitted thereby subsequent to the start of irradiation of the exciting light to attain 90% of the maximum intensity thereof is about 100  $\mu\text{sec}$ . Also, the fall time  $t_d$  required for the intensity of the fluorescent afterglow subsequent to the interruption of irradiation of the exciting light to attenuate by a quantity corresponding to 80% of the maximum intensity of the fluorescent light is about 50  $\mu\text{sec}$ . Thus, both of the rise time  $t_r$  and the fall time  $t_d$  are smaller than 200  $\mu\text{sec}$ , showing an extremely high response.

[0084] Fig. 3(c) illustrates the condition of emission of the fluorescent light from the fluorescent substance which is  $\text{LiNd}_{0.5}\text{Yb}_{0.5}\text{P}_4\text{O}_{12}$ , showing that the rise time  $t_r$  is about 1,300  $\mu\text{sec}$  and the fall time  $t_d$  is about 1,000  $\mu\text{sec}$ , both of them being considerably greater than 200  $\mu\text{sec}$ . If the rise time  $t_r$  of the fluorescent substance is smaller than 200

μsec as discussed above, the length of time required for the light receiving element to receive light subsequent to the start of irradiation of the exciting light is extremely small and, accordingly, a reading of a fluorescent mark formed by the use of the fluorescent substance can be accomplished at a high speed.

**[0085]** Also, when as shown in Fig. 4 information is to be read out by an optical reading apparatus 25 from a fluorescent mark in the form of a pattern of bar codes defined by fluorescent ink deposits 18 formed by printing a fluorescent inking medium while a fluorescent mark carrier 10 bearing such fluorescent mark is transported in one direction, the fluorescent substance contained in each fluorescent ink deposit 18 is activated by irradiating the fluorescent mark by the exciting light 60 emitted from the light emitting element incorporated in the optical reading apparatus 25 to cause the fluorescent substance to emit from the respective ink deposit 18 the fluorescent light 61 which is subsequently received by the light receiving element in the optical reading apparatus 25 for reading of the bar code information.

**[0086]** It is to be noted that reference numeral 32 represents a slit member disposed on an optical path through which, as will become clear from the subsequent description, the exciting light 60 is projected onto the fluorescent ink deposits 18 one at a time and the resultant fluorescent light 61 from the respective fluorescent ink deposit 18 travels towards the light receiving element in the optical reading apparatus 25. Assuming that the speed  $v$  of transport of the fluorescent mark carrier 10 is expressed by  $v$ , the length of a slit 32a defined in the slit member 32 as measured in a direction conforming to the direction of transport is expressed by  $d$  and the rise time of the fluorescent substance is expressed by  $t_u$ , and if arrangement is made to establish the relationship of  $(t_u \leq d/v)$ , information represented by each fluorescent ink deposit 18 on the fluorescent mark carrier being transported can assuredly be read only when such fluorescent ink deposit 18 is brought into alignment with the slit 32a of the slit member 32. If, however, the rise time  $t_u$  of the fluorescent substance is greater than  $d/v$ , the respective ink deposit 18 will pass underneath the slit 32a without giving rise to a sufficient intensity of the fluorescent light and, accordingly, the light receiving element will provide an output so low as to result in a problem in reliability.

**[0087]** Also, referring still to Fig. 4, if arrangement is made to establish the relationship of  $(t_d \leq L/v)$  wherein  $L$  represents the interval between the neighboring fluorescent ink deposits (for example, bars) 18 as measured in a direction conforming to the direction of transport of the fluorescent mark carrier 10 and  $t_d$  represents the fall time of the fluorescent substance, an accurate reading of the bar code information is possible. If the fluorescent substance having a relatively long fall time  $t_d$ , that is, the fluorescent substance capable of giving a fluorescent afterglow for a relatively long time, is employed, the fluorescent afterglow emanating from one of the fluorescent ink deposits 18 that precedes the fluorescent ink deposit 18 having moved past a position aligned with the slit 32a may also be read and, therefore, an accurate reading of the code information cannot be accomplished.

**[0088]** In contrast thereto, the use of the fluorescent substance having the fall time  $t_d$  that is extremely small as shown in Fig. 3(b) is employed, the problem such as discussed above can be eliminated, making it possible to accomplish an accurate reading of the code information and also to reduce the interval  $L$  between the neighboring ink deposits forming the code bars to thereby reduce the area in which the fluorescent mark is formed.

**[0089]** The use of an organic binder having a density  $\rho_2$  which satisfies the relationship of  $(\rho_1/\rho_2 \leq 1.8)$  wherein  $\rho_1$  represents the density of the fluorescent substance is effective to eliminate such a problem that the amount sediment of the fluorescent microparticles in the inking medium is so small that, when the fluorescent ink deposit is formed, the fluorescent microparticles may be concealed having been covered by a film of binder to an extent as to prevent the fluorescent light from being quickly surfaced.

**[0090]** The content of the binder in the fluorescent ink deposit must be equal to or greater than 5 wt%. If the content of the binder is smaller than 5 wt%, the fluorescent particles may separate and, for this reason, printing of the bar code will become incomplete to such an extent as to pose a difficulty in properly retaining the information. In view of this, the content of the binder is required to be equal to or greater than 5 wt%.

**[0091]** For a water-soluble organic binder, acrylic resin or an acrylic resin having, in its side chain, an ester group or polyether may be employed. Other than these examples, polyvinyl alcohol, polyvinyl pyrrolidone, carboxymethylcellulose, starch, a formalin condensate of naphthalene sulfonate or polystyrene sulfonate may also be employed.

**[0092]** For a non-water-soluble organic binder, a phenol resin such as, for example, novolak-type phenol, resol-type phenol, rosin-modified phenol or alkyl-modified phenol, a water-added rosin or a rosin resin such as, for example, polyethylene glycol ester, polyfunctional alcohol ester or rosin glycerin ester may be employed.

**[0093]** For a solvent, one or a mixture of water, alcohol, ketone, ester, ether, a solvent of aromatic hydrocarbon and a solvent of fatty hydrocarbon may be employed.

**[0094]** An electrolyte used as a electroconductivity imparting agent may be  $\text{LiNO}_3$ ,  $\text{LiCl}$ ,  $\text{KCl}$ ,  $\text{NaCl}$  or  $\text{KNO}_3$ .

**[0095]** For a stabilizer, one or a mixture of alkyl phthalate (for example, dioctyl phthalate or dibutyl phthalate), aryl phthalate, glycol (ethylene glycol, propylene glycol, polyethylene glycol or polypropylene glycol) and glycol ester may be employed.

**[0096]** A defoaming agent used may be a silicone type, a silica-silicone type, a metallic soap, an amide type, or a polyether type.

**[0097]** One or more dyes may also be employed. Examples of the dyes include Direct Black GW, Capamine® Black

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ESA, Rodamine® B, Rodamine® 7G, methylene blue, Direct Fast Orange, Complantine® Green G, Milling Yellow O and Katione® Pink FG.

**[0098]** A specific composition of the inking medium for use with an ink jet printer will now be illustrated.

5	Complex salt of cinnamic acid with neodymium and ytterbium (0.2 in average particle size)	80 parts by weight
	Phthalocyanine blue	1 part by weight
10	Cation-type acrylic resin	20 parts by weight
	Polyethylene glycol	1 part by weight
	Diethyl phthalate	0.5 part by weight
15	KCl	0.5 part by weight
	Defoaming agent	0.4 part by weight
20	Water	100 parts by weight
	Ethanol	20 parts by weight

25 **[0099]** The composition was mixed and dispersed in a sand mill for one hour to provide the fluorescent inking medium for use with the ink jet printer which was subsequently used in the ink jet printer to accomplish a printing of characters on a paper.

**[0100]** Observation on the printed characters has indicated that no ink run occurred and that the characters were printed precisely in a blue color.

30 **[0101]** To detect the printed characters optically, 100 identical reading tests were carried out at a reading speed of 4 m/sec by irradiating the printed characters by the exciting light having a maximum intensity in the vicinity of a wavelength of 970 nm to emit fluorescent light which was then received by a silicon photodiode detector. As a result, the information was assuredly read out each time the reading test was conducted.

35 **[0102]** It is to be noted that in the above described composition of the inking medium, the amount of any one of phthalocyanine blue, polyethylene glycol, diethyl phthalate, water and ethanol added may be either increased or decreased if desired and that the use of one or more of them may be dispensed with if desired.

40 **[0103]** As listed in the above table of composition of the inking medium, if where water is employed for the solvent an easily volatilizeable organic liquid such as, for example, alcohol having a compatibility with water is employed in combination with water, the resultant fluorescent composition is quick to dry and is, therefore, effectively utilized when such fluorescent composition is to be printed on, for example, papers and, in particular, where a relatively large amount of the solvent is employed such as that used with the ink jet printer.

45 **[0104]** In the above described composition of the inking medium, using different inking mediums of a substantially identical composition, but in which the quantity of cation-type acrylic resin added was varied to provide a differing viscosity, the relationship among the viscosity of each inking medium, the degree of variability of the size of droplets of the respective inking medium and the relative emission output of the fluorescent ink deposit formed by the use of the respective inking medium was examined, a result of which is shown in Fig. 5.

50 **[0105]** As can readily be understood from Fig. 5, when the viscosity of the inking medium for use with the ink jet printer is within the range of 2 to 25 cps and preferably within the range of 10 to 20 cps, the degree of variability of the ink droplet size is smaller than 10% indicating that the ink droplets of a substantially uniform size could be obtained sufficient to result in an excellent printability and, also, a sufficient emission output could be obtained.

**[0106]** In the above described composition of the inking medium, using different inking mediums of a substantially identical composition, but in which the quantity of ethanol added was varied to provide a differing surface tension, the relationship between the surface tension of each inking medium and the degree of variability of the size of droplets of the respective inking medium was examined, a result of which is shown in Fig. 6.

55 **[0107]** As can readily be understood from Fig. 6, when the surface tension of the inking medium for use with the ink jet printer is within the range of 23 to 4-dyne/cm and preferably within the range of 26 to 37 dyne/cm, the degree of variability of the size of the ink droplets is small and the ink droplets of a uniform size required by the ink jet printer could be obtained accompanied by an excellent printability.

[0108] In the above described composition of the inking medium, using different inking mediums of a substantially identical composition, but in which the quantity of the electrolyte (KCl) added was varied to provide a differing specific resistance, the relationship between the specific resistance of each inking medium and the degree of variability of the size of droplets of the respective inking medium was examined, a result of which is shown in Fig. 7.

[0109] As can readily be understood from Fig. 7, when the specific resistance of the inking medium for use with the ink jet printer is equal to or lower than 2,000  $\Omega$ -cm and preferably equal to or lower than 1,500  $\Omega$ -cm, the degree of variability of the size of the ink droplets is small and the ink droplets of a uniform size required by the ink jet printer could be obtained accompanied by an excellent printability. It is, however, to be noted that if the specific resistance of the inking medium for use with the ink jet printer exceeds 2,000  $\Omega$ -cm, and if the ink jet printer is particularly of a charged deflection printing system, control of deflection of the ink droplets will become difficult to accomplish, resulting in a reduction in print quality with flaws and/or skews appearing in the printed characters.

[0110] In the above described composition of the inking medium, using different inking mediums of a substantially identical composition, but in which KOH was added in addition to KCL and the quantity of KOH added was varied to provide a differing pH value, the relationship between the pH value and the dispersion stability of the respective inking medium was examined, a result of which is shown in Fig. 8. It is to be noted that the dispersion stability is expressed in terms of the percentage of a supernatant liquid relative to the total amount of the respective inking medium, which supernatant liquid was obtained after the respective inking medium had been allowed to stand for one week.

[0111] As can readily be understood from Fig. 8, when the pH value of the inking medium is within the range of 4.5 to 10 and preferably within the range of 5 to 7, both the dispersibility and the dispersion stability of the inking medium are extremely satisfactory. It is, however, to be noted that if the pH value of the inking medium for use with the ink jet printer is smaller than 4.5 or greater than 10, the dyes used in the inking medium tend to coagulate.

[0112] Thus, when the inking medium of the present invention for use with an ink jet printer is prepared to a viscosity within the range of 2 to 25 cps, a surface tension within the range of 23 to 40 dyne/cm, a specific resistance not higher than 2,000  $\Omega$ -cm and a pH value within the range of 4.5 to 10, the inking medium excellent in dispersion stability, substantially free from ink run, excellent in printability and high in emission output can be obtained.

[0113] Hereinafter, the fluorescent substance of the present invention will be illustrated by way of examples.

#### Example 1

[0114] 1 part by weight of complex salt of cinnamic acid with neodymium and ytterbium was suspended in 20 parts by weight of water and was then, while being stirred, added dropwise with a solution prepared by dissolving 0.005 part by weight of anthraquinone dyestuff ("IR 750" available from Nippon Kayaku Kabushiki Kaisha. Absorption peak at 750 nm) into 1 part by weight of DMF. After one hour stirring, the mixture was filtered and dried to obtain the infrared-excitable fluorescent substance.

#### Example 2

[0115] 1 part by weight of complex salt of cinnamic acid with neodymium and ytterbium was suspended in 20 parts by weight of water and was then, while being stirred, added dropwise with a solution prepared by dissolving 0.003 part by weight of polymethine dyestuff ("IR-820B" available from Nippon Kayaku Kabushiki Kaisha. Absorption peak at 820 nm) into 1 part by weight of DMF. After one hour stirring, the mixture was filtered and dried to obtain the infrared-excitable fluorescent substance.

#### Example 3

[0116] 1 part by weight of ytterbium benzoate was suspended in 20 parts by weight of water and was then, while being stirred, added dropwise with a solution prepared by dissolving 0.003 part by weight of polymethine dyestuff ("IR-820B" available from Nippon Kayaku Kabushiki Kaisha. Absorption peak at 820 nm) into 1 part by weight of DMF. After one hour stirring, the mixture was filtered and dried to obtain the infrared-excitable fluorescent substance.

#### Comparison 1

[0117] The infrared-excitable fluorescent substance was prepared by pulverizing  $\text{LiNd}_{0.5}\text{Yb}_{0.5}\text{P}_4\text{O}_{12}$  with the use of a ball mill.

#### Comparison 2

[0118] The infrared-excitable fluorescent substance was obtained in a manner similar to Example 1, except that the

anthraquinone dye ("IR 750) used in Example 1 was not employed.

#### (High Speed Reading Test)

[0119] Each of the infrared-excitable fluorescent substances obtained under Examples 1 to 3 and Comparisons 1 and 2 was molded into a respective disc testpiece of 5 mm in diameter and 2 mm in thickness. A high speed reading test was carried out by scanning the testpiece at a speed of 8 m/sec, irradiating the testpiece by means of a commercially available GaAlAs light emitting diode and detecting the fluorescent light by means of a Si-PIN photodetector capable of detecting light of 970 nm. The exciting light emitted from the GaAlAs light emitting diode was of a wavelength varying depending on the exciting wavelength of the organic material (the wavelength of the exciting light required for the organic material to emit fluorescent light) so far as the respective fluorescent substances of Examples 1 to 3 are concerned. An optical filter ("IR-94" available from Fuji Photo Film Co., Ltd.) was placed in front of the photodetector. The result of the high speed reading test conducted on each of those fluorescent substances is shown in Table 1 below.

Table 1

	Exciting Wavelength (nm)	Relative Intensity (%)
Example 1	760	700
Example 2	800	650
Example 3	760	800
Comp. 1	800	Failed
Comp. 2	800	100

[0120] Using the specific fluorescent substance and the specific binder, a fluorescent inking medium was prepared in the following manner.

#### Example 4

[0121] complex salt of cinnamic acid with neodymium and ytterbium 1 parts by weight

Anthraquinone dyestuff (IR 750)	0.005 part by weight
PVA	4 parts by weight
Water/EtOH (8/2)	20 parts by weight

[0122] This composition was dispersed for 24 hours in a ball mill to provide the inking medium which was subsequently loaded in an ink jet printer to for a fluorescent mark.

#### Comparison 3

[0123] A fluorescent mark was formed in a manner similar to Example 4, except that the complex salt of cinnamic acid with neodymium and ytterbium used in Example 4 was not used.

#### Comparison 4

[0124] A fluorescent mark was formed in a manner similar to Example 4, except that the anthraquinone dyestuff (IR 750) used in Example 4 was not used. However, in Table 2 below, the fluorescent mark irradiated by the exciting wavelength of 760 nm and the fluorescent mark irradiated by the exciting wavelength of 800 nm are identified by (a) and (b), respectively.

#### Example 5

[0125]

Ytterbium cinnamate	1 parts by weight
Polymethine dyestuff (IR 820)	0.003 part by weight
PVA	4 parts by weight

(continued)

Water/EtOH (8/2)	20 parts by weight
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- 5 [0126] This composition was dispersed for 24 hours in a ball mill to provide the inking medium which was subsequently loaded in an ink jet printer to for a fluorescent mark.

**Comparison 5**

- 10 [0127] A fluorescent mark was formed in a manner similar to Example 5, except that the polymethine dyestuff (IR 820) used in Example 5 was not used.

**Comparison 6**

- 15 [0128] A fluorescent mark was formed in a manner similar to Example 5, except that the ytterbium cinnamate used in Example 5 was not used.

**Example 6**

- 20 [0129]

Ytterbium benzoate	1 parts by weight
Polymethine dyestuff (IR 820)	0.005 part by weight
PVA	4 parts by weight
Water/EtOH (8/2)	20 parts by weight

- 25 [0130] This composition was dispersed for 24 hours in a ball mill to provide the inking medium which was subsequently loaded in an ink jet printer to for a fluorescent mark.

**Comparison 7**

- 30 [0131] A fluorescent mark was formed in a manner similar to Example 6, except that the polymethine dyestuff (IR 820) used in Example 6 was not used.

**Comparison 8**

- 35 [0132] A fluorescent mark was formed in a manner similar to Example 6, except that the ytterbium benzoate used in Example 6 was not used.

**(High Speed Reading Test)**

- 40 [0133] Printed matter prepared by the use of each of the infrared-excitable fluorescent substances obtained under Examples 4 to 6 and Comparisons 3 to 7 was subjected to a high speed reading test. This high speed reading test was carried out by scanning the testpiece at a speed of 8 m/sec, irradiating the testpiece by means of a commercially available GaAlAs light emitting diode and detecting the fluorescent light by means of a Si-PIN photodetector capable of detecting light of 970 nm. The exciting light emitted from the GaAlAs light emitting diode was of a wavelength varying depending on the exciting wavelength of the organic material so far as the printed matters under Examples 4 to 6 and Comparisons 3, 6 and 8 are concerned. An optical filter ("IR-94" available from Fuji Photo Film Co., Ltd.) was placed in front of the photodetector. The result of the high speed reading test conducted on each of those printed matters is shown in Table 1 below.

Table 2

	Exciting Wavelength (nm)	Relative Intensity (%)
Example 4	760	100
Example 5	800	100
Example 6	800	120



Table 2 (continued)

	Exciting Wavelength (nm)	Relative Intensity (%)
Comp. 3	760	30
Comp. 4 (a)	760	Failed
Comp. 4 (a)	800	40
Comp. 5	800	20
Comp. 6	800	10
Comp. 7	800	10
Comp. 8	800	40

[0134] As Tables 1 and 2 make it clear, the fluorescent substance obtained under each of Examples 1 to 3 results in a sufficient emission output during the high speed reading as compared with that under each of Comparisons 1 and 2. Also, the fluorescent substance obtained under each of Examples 1 to 3 can be excited to emit a fluorescent light in response to a varying exciting wavelength.

[0135] The inking medium obtained under each of Examples 4 to 6 is suited for use with the ink jet printer.

#### Fluorescent Mark Carrier

[0136] The carrier on which the fluorescent composition is deposited to complete the fluorescent mark carrier may be a security, a sales slip, an invoice, a card, a book, a surface of merchandise or any other member on which ink droplets can deposit.

[0137] As a result of examination conducted on the content of the fluorescent particles in the fluorescent ink deposit (i.e., the amount of the fluorescent particles relative to the total weight of the fluorescent ink deposit, it has been found that unless the content of the fluorescent particles is smaller than 1 wt% relative to the weight of the fluorescent ink deposit on the carrier, no intended emission intensity can be obtained. Although increase of the content of the fluorescent particles result in a gradual increase of the emission intensity, the fluorescent particles would aggregate or overlap densely with the emission density no longer increasing if the content of the fluorescent particles exceeds 50 wt%. Specifically, if the content of the fluorescent particles exceeds 30 wt%, the fluorescent ink deposit on the carrier would become noticeable in sight and, particularly where the fluorescent particles made up of the inorganic compound of a relatively large particle size, the printability exhibited by the ink jet printer or a screen printing technique would be lowered.

[0138] Accordingly, when the content of the fluorescent particles in the fluorescent deposit is controlled to greater than 1 wt%, but smaller than 30 wt%, a desired emission density can be maintained without allowing the fluorescent ink deposit to be noticeable in sight and, therefore, the appearance of the fluorescent mark carrier will not be adversely affected, accompanied by a satisfactory printability. This content is particularly advantageous in the case where the fluorescent particles used have an average particle size not greater than 4  $\mu\text{m}$  and preferably not greater than 2  $\mu\text{m}$  discussed hereinbefore.

[0139] As a result of studies conducted on the relationship between the thickness of the fluorescent ink deposit and the average particle size of the fluorescent particles used, it has been found that, if the thickness of the fluorescent ink deposit is controlled to a value smaller than 35 times, or preferably 25 times, the average size of the fluorescent particles, the presence of the fluorescent ink deposit forming a fluorescent mark on the carrier would neither substantially be felt to the touch nor become noticeable in sight and, for this reason, the appearance of the fluorescent mark carrier would not be adversely affected. Accordingly, in the practice of the present invention, it is preferred that if the average particle size of the fluorescent particles is 4  $\mu\text{m}$  or 2  $\mu\text{m}$ , the thickness of the fluorescent ink deposit should be not greater than 140  $\mu\text{m}$  or 70  $\mu\text{m}$ , respectively.

[0140] As a result of studies conducted on the light transmission exhibited by the binder used to disperse and retain the fluorescent particles, it has been found that if the transmittance of the exciting and fluorescent light is higher than 80%, and preferably 90%, penetration of the exciting light into the fluorescent ink deposit and emission of the fluorescent light outwardly from the fluorescent ink deposit take place efficiently, exhibiting a relatively high emission output sufficient to accomplish an assured detection of the fluorescent mark.

[0141] The inventors have conducted a series of studies on the surface condition of the fluorescent ink deposit. Comparison has been made between the emission output exhibited when a paint containing the fluorescent particles of the present invention was applied to a film of synthetic resin to form the fluorescent ink deposit and that when the same paint was applied to a paper to form the fluorescent ink deposit and, as a result of the comparison, it has been found that the paper having the fluorescent ink deposit thereon exhibited a relatively high emission output.

[0142] While visual inspection of the surface condition of the fluorescent ink deposit formed on the film of synthetic

resin has indicated that the surface of the fluorescent ink deposit was smooth, the fluorescent ink deposit formed on the paper has shown that the surface thereof contained minute surface irregularities. Because of the presence of the minute surface irregularities, the exciting light impinging upon the fluorescent ink deposit does not undergo a specular reflection and appeared to have participated in activation of the fluorescent substance and, therefore, a relatively high emission output would have been obtained. In particular, where the average particle size of the fluorescent particles is smaller than the fiber diameter of fibrous material forming the paper (for example, if the average particle size is about 0.2  $\mu\text{m}$ ), the efficiency of excitation of the fluorescent substance is high because the fluorescent particles deposit at a varying angle on surfaces of fibers intertwined randomly and irregularly.

[0143] Where the fluorescent ink deposit is to be formed on an item to be delivered such as a postal matter or a parcel, or a card such as a pre-paid card or a commutation card as will be described later, it is recommended that the resultant fluorescent deposit will not be noticeable in sight. In order for the fluorescent ink deposit to be unnoticeable in sight, one method to accomplish this is to restrict the thickness of the fluorescent ink deposit, but restriction of the absorption of visible rays of light is also effective to accomplish this.

[0144] The principal component of the fluorescent ink deposit is a mixture of the binder and the fluorescent particles and, therefore, if the binder and the fluorescent particles both having a low absorptivity with respect to the visible rays of light are used so that the absorptivity of the fluorescent ink deposit eventually formed with respect to the visible rays of light may be restricted to a value lower than 20% and preferably lower than 10%, it has been found that the fluorescent ink deposit can be made substantially colorless and nearly transparent and, therefore, the appearance of the fluorescent mark carrier would not be adversely affected.

[0145] With the fluorescent mark carrier according to an embodiment of the present invention, the fluorescent ink deposits formed thereon will not be copied onto a transfer paper or will be copied onto a transfer paper in a manner not noticeable in sight when an attempt is made to make a copy of it and, therefore, there is no possibility that the transfer paper would be stained by images of the fluorescent ink deposits on the fluorescent mark carrier.

[0146] A specific example, in which the fluorescent mark containing the fluorescent composition is formed on a postal envelope or a postal card is shown in Fig. 9.

[0147] As shown in Fig. 9, a postal matter 13 such as, for example, a postal envelope, a postal card or a postal tag attached to a parcel has a front surface on which not only is a postal stamp 14 attached, but also a zip code 15, an address 16 and an addressee 17 are written down. In addition to those items present on the front surface of the postal matter 13, bar code information associated with the address is printed on a predetermined area by the ink jet recording system to form the fluorescent ink deposits 18. Since the bar code information is represented by the fluorescent mark not visible under visible rays of light, the appearance of the postal matter 13 will not be adversely affected.

[0148] Another example of the postal matter 13 is shown in Fig. 10. In this example, the bar code associated with the address is printed on a label 19 in the form of the fluorescent mark, which label 19 is, when the addresser intends to post the postal matter 13, affixed to a predetermined area of the postal matter 13 before the latter is submitted to a post office. It is to be noted that if the area to which the label 19 is to be affixed varies from one postal matter to another, information reading would be hampered and, therefore, the postal matter 13 has a blank box printed at that area so that the position where the label 19 is to be affixed can be specified.

[0149] While reference has been made to the postal matter, a similar description equally applies to any other matter desired to be delivered such as, for example, a parcel to be delivered by a courier or an in-house mail.

[0150] Also, while the information such as the address, the addressee and so on has been shown as printed with the use of the fluorescent composition, other information such as the address of the sender, the addresser's name may also be printed.

[0151] Fig. 11 illustrates a flowchart explanatory of the process of imparting and reading the bar code information to and from the postal matter 13.

[0152] Postal matters 13 collected at a post office are first put into a rectifying machine so that the postal matters 13 can be rectified so as to orient in a predetermined direction. Since some of the postal matters 13 have a label 19 affixed thereto and the others do not have, the postal matters 13 are classified by a classifying machine into two groups, one including the postal matters 13 having no label and the other including the postal matters 13 with labels 19 affixed thereto. This classification can be accomplished by irradiating the predetermined area of each postal matter 13 where the label 19 ought to be affixed. Should a fluorescent light from the predetermined area of some of the postal matters 13 be detected, it is clear that such some of the postal matters 13 have a label 19 affixed thereto, or otherwise the postal matters 13 would be deemed having no label 19.

[0153] The postal matters 13 having no label 19 affixed thereto are transferred to an optical character recognizing machine (OCR) 22 where the zip code 15 and the address 16 are optically read out. Based on the information read out by the OCR 22, the bar code information associated with the address is printed by an ink jet printer (IJP) 23 on the predetermined area of each of the postal matters 13.

[0154] Both of the postal matters 13 having no label 19 affixed thereto, but the bar code information printed thereon and the postal matters 13 having the labels 19 affixed thereto are subsequently transferred onto a bar code sorting

machine 24 by which the bar code information is optically read out so that the postal matters 13 can be subsequently sorted according to the bar code information.

[0155] The bar code sorting machine 24 referred to above may generally comprise an optical reading apparatus for optically reading the bar code information and a sorting apparatus for sorting the postal matters 13 according to the bar code information read out by the optical reading apparatus.

## INDUSTRIAL APPLICABILITY

[0156] The optical reading system of the present invention is applicable in the following applications and has the following features.

### a) Factory Automation:

During automobile assemblage, car management, that is, classification of car according to the brand, export destination, date of manufacture and/or product lot number, can be accomplished using a fluorescent mark without adversely affecting the appearance of each car.

b) Even if the fluorescent marking is printed on a black-color item such as tires or on a transparent item of glass or synthetic resin, which has hitherto been unable to read with the prior art reflective bar code, the mark can be assured read out.

c) Since even if any ornamental design is printed over the fluorescent mark, such fluorescent mark can readily be read out, a plurality of pieces of information can be overlapped one above the other and, therefore, a limited space such as found in a price tag or a product tag of the merchandise can be effectively utilized.

d) By a reason similar to (a) and (b) above, effective utilization is possible to products such as cosmetics and medicines, the design of which is considered of importance, or to boxes or packages which are required for a high quality sensation to be appealing.

e) Even under the environment in which the prior art reflective bar code cannot be used due to the presence of oil and dust such as found in a factory or plant, the fluorescent mark can assuredly be read out.

f) By a reason similar to (a) and (b) above, for the convenience on the part of a manufacturer, a concealed code may be provided on invoices issued to clients for management purpose. (In general, the invoices are specified by clients or of a format in which a client writes down.)

g) Information may be provided on a card-like item as a concealed code so that the card-like item can be used as a game card (bar code game).

h) By a reason similar to (a) and (c), if used in connection with management of books, literature or drawings, the design will not be adversely affected.

i) Not only can any possible forgery of a student's certificate or an ID card be prevented, but also the certificate or ID card can be reduced in size or space.

k) Not only can any possible forgery of a stamp card or a point card be prevented, but also the card can be reduced in size or space.

l) Any possible forgery can be prevented by introducing the system of the invention in a Pachinko gift-exchange system.

## Claims

1. A fluorescent substance of a kind capable of emitting, in response to irradiation of exciting light, a fluorescent light of a wavelength different from that of the exciting light, characterized in that the average particle size of the fluorescent substance is smaller than the wavelength of the fluorescent light at the maximum intensity of such fluorescent light emitted by such fluorescent substance.

2. A fluorescent substance of a kind capable of emitting, in response to irradiation of exciting light, a fluorescent light of a wavelength different from that of the exciting light, characterized in that the average particle size of the fluorescent substance is smaller than the wavelength of the fluorescent light at the maximum intensity of the exciting light.

3. The fluorescent substance as defined in Claim 1 or 2, characterized in that the average particle size of the fluorescent substance is not greater than 0.8  $\mu\text{m}$ .

4. The fluorescent substance as defined in any one of Claims 1 to 3, characterized in that the fluorescent substance is an organic metallic compound containing at least Nd as an optical active element.

5. The fluorescent substance as defined in Claim 4, characterized in that the organic metallic compound contains at least one organic material selected from the group consisting of carboxylic acid, ketone, ether and amine.
- 5 6. The fluorescent substance as defined in Claim 4, characterized in that the organic metallic compound is at least one organic material selected from the group consisting of neodymium cinnamate, complex salt of cinnamic acid with neodymium and ytterbium, complex salt of benzoic acid with neodymium and ytterbium, neodymium naphthoate, and complex salt of naphthoeic acid with neodymium and ytterbium.
- 10 7. The fluorescent substance as defined in Claim 4, characterized in that the fluorescent substance contains Nd and Yb, the molar ratio of Nd relative to Yb (Nd:Yb) being within the range of 9:1 to 5:5.
8. The fluorescent substance as defined in any one of Claims 1 to 7, characterized in that the rise time required for the intensity of the fluorescent substance to reach 90% of the maximum intensity thereof subsequent to irradiation of the exciting light is within 200  $\mu$ sec.
- 15 9. The fluorescent substance as claimed in any one of Claims 1 to 8, characterized in that the fall time required for the intensity of the fluorescent light to attenuate 80% of the maximum intensity thereof subsequent to interruption of the irradiation is within 200  $\mu$ sec.
- 20 10. A fluorescent composition characterized in that it comprises a fluorescent substance in the form of ultra-microparticles capable of emitting a fluorescent light of a wavelength different from that of an exciting light and having an average particle size smaller than the wavelength of the maximum intensity of the fluorescent light, a binder transparent to both of the exciting light and the fluorescent light, and a solvent.
- 25 11. A fluorescent composition characterized in that it comprises a fluorescent substance in the form of ultra-microparticles capable of emitting a fluorescent light of a wavelength different from that of an exciting light and having an average particle size smaller than the wavelength of the maximum intensity of the exciting light, a binder transparent to both of the exciting light and the fluorescent light, and a solvent.
- 30 12. The fluorescent composition as defined in Claim 10 or 11, characterized in that the fluorescent composition is used as an inking medium for an ink jet printer.
13. The fluorescent composition as defined in any one of Claims 10 to 12 characterized in that the fluorescent substance is comprised of an organic metallic compound.
- 35 14. The fluorescent composition as defined in Claim 13 characterized in that an organic material contained in the organic metallic compound is at least one element selected from the group consisting of carboxylic acid, ketone, ether and amine.
- 40 15. The fluorescent composition as defined in Claim 13, characterized in that the organic metallic compound is at least one organic material selected from the group consisting of neodymium cinnamate, complex salt of cinnamic acid with neodymium and ytterbium, complex salt of benzoic acid with neodymium and ytterbium, neodymium naphthoate, and complex salt of naphthoeic acid with neodymium and ytterbium.
- 45 16. The fluorescent composition as defined in Claim 13 characterized in that the fluorescent substance contains Nd and Yb, the molar ratio of Nd relative to Yb (Nd:Yb) being within the range of 9:1 to 5:5.
17. The fluorescent composition as defined in any one of Claims 10 to 16 characterized in that the density  $\rho_1$  of the fluorescent substance and the density  $\rho_2$  of the binder have a relationship of  $\rho_1/\rho_2 \leq 1.8$ .
- 50 18. The fluorescent composition as defined in any one of Claims 10 to 16 characterized in that the fluorescent composition has a viscosity within the range of 2 to 25 cps.
19. The fluorescent composition as defined in any one of Claims 10 to 16 characterized in that the fluorescent composition has a surface tension within the range of 23 to 40 dyne/cm.
- 55 20. The fluorescent composition as defined in any one of Claims 10 to 16, characterized in that the fluorescent composition has a specific resistance not higher than 2,000  $\Omega$ cm.

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21. The fluorescent composition as defined in any one of Claims 10 to 16, characterized in that the fluorescent composition has a pH value within the range of 4.5 to 10.
- 5 22. The fluorescent composition as defined in any one of Claims 10 to 16, characterized in that the binder is a water-soluble resin.
23. The fluorescent composition as defined in Claim 22, characterized in that the solvent is water and an easily volatilizeable liquid compatible with water.
- 10 24. The fluorescent composition as defined in any one of Claims 10 to 16, characterized in that the binder has a light transmittance of not lower than 80% relative to both of the exciting light and the fluorescent light.
25. The fluorescent composition as defined in any one of Claims 10 to 16, characterized in that the binder is a non-water-soluble resin.
- 15 26. The fluorescent composition as defined in any one of Claims 10 to 16, characterized in that the fluorescent substance is of a kind having a rise time, required for the intensity of the fluorescent light to attain 90% of the maximum intensity thereof subsequent to start of irradiation of the exciting light, which is within 200  $\mu$ sec.
- 20 27. The fluorescent composition as defined in any one of Claims 10 to 16 and 26 characterized in that the fluorescent substance is of a kind having a fall time required for the intensity of the fluorescent light to attenuate 80% of the maximum intensity thereof subsequent to interruption of the irradiation, which is within 200  $\mu$ sec.
- 25 28. The fluorescent composition as claimed in any one of Claims 10 to 16, characterized in that a dyestuff is added.
29. A fluorescent mark carrier characterized in that it has a fluorescent ink deposit formed thereon, said fluorescent ink deposit containing a fluorescent substance capable of emitting a fluorescent light of a wavelength different from that of the exciting light and having an average particle size smaller than the wavelength of the maximum intensity of the fluorescent light is printed thereon.
- 30 30. A fluorescent mark carrier characterized in that it has a fluorescent ink deposit formed thereon, said fluorescent ink deposit containing a fluorescent substance capable of emitting a fluorescent light of a wavelength different from that of the exciting light and having an average particle size smaller than the wavelength of the maximum intensity of the exciting light is printed thereon.
- 35 31. The fluorescent mark carrier as defined in Claim 29 or 30, characterized in that the fluorescent ink deposit is formed by an ink jet printer.
- 40 32. The fluorescent mark carrier as defined in any one of Claims 29 to 31, characterized in that the fluorescent substance is comprised of an organic metallic compound.
33. The fluorescent mark carrier as defined in Claim 32, characterized in that an organic material contained in the organic metallic compound is at least one element selected from the group consisting of carboxylic acid, ketone, ether and amine.
- 45 34. The fluorescent mark carrier as defined in Claim 33, characterized in that the organic metallic compound is at least one organic material selected from the group consisting of neodymium cinnamate, complex salt of cinnamic acid with neodymium and ytterbium, complex salt of benzoic acid with neodymium and ytterbium, neodymium naphthoate, and complex salt of naphthoeic acid with neodymium and ytterbium.
- 50 35. The fluorescent mark carrier as defined in Claim 32, characterized in that the fluorescent substance contains Nd and Yb, the molar ratio of Nd relative to Yb (Nd:Yb) being within the range of 9:1 to 5:5.
- 55 36. The fluorescent mark carrier as defined in Claim 29 or 30, characterized in that the fluorescent ink deposit contains a binder in a quantity not smaller than 5 wt%.

Patentansprüche

1. Fluoreszierende Substanz einer Art, die - als Antwort auf die Bestrahlung mit anregendem Licht - befähigt ist, fluoreszierendes Licht einer Wellenlänge zu emittieren, die von derjenigen des anregenden Lichts verschieden ist, dadurch gekennzeichnet, daß die durchschnittliche Teilchengröße der fluoreszierenden Substanz kleiner ist als die Wellenlänge des fluoreszierenden Lichts bei der maximalen Intensität eines solchen fluoreszierenden Lichts, das durch eine solche fluoreszierende Substanz abgegeben wird.
2. Fluoreszierende Substanz einer Art, die - als Antwort auf die Bestrahlung mit anregendem Licht - befähigt ist, fluoreszierendes Licht einer Wellenlänge zu emittieren, die von derjenigen des anregenden Lichts verschieden ist, dadurch gekennzeichnet, daß die durchschnittliche Teilchengröße der fluoreszierenden Substanz kleiner ist als die Wellenlänge des fluoreszierenden Lichts bei der maximalen Intensität des anregenden Lichts.
3. Fluoreszierende Substanz gemäß den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß die durchschnittliche Teilchengröße der fluoreszierenden Substanz nicht größer als 0,8 µm ist.
4. Fluoreszierende Substanz gemäß irgendeinem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die fluoreszierende Substanz eine metallorganische Verbindung ist, die wenigstens Nd als optisch-aktives Element enthält.
5. Fluoreszierende Substanz gemäß Anspruch 4, dadurch gekennzeichnet, daß die metallorganische Verbindung wenigstens ein organisches Material enthält, das aus der aus Carbonsäure, Keton, Ether und Amin bestehenden Gruppe ausgewählt ist.
6. Fluoreszierende Substanz gemäß Anspruch 4, dadurch gekennzeichnet, daß die metallorganische Verbindung wenigstens ein organisches Material ist, das aus der aus Neodymcinnamat, Komplexsalz aus Zimtsäure mit Neodym und Ytterbium, Komplexsalz aus Benzoesäure mit Neodym und Ytterbium, Neodymnaphthoat und Komplexsalz aus Naphthoesäure mit Neodym und Ytterbium bestehenden Gruppe ausgewählt ist.
7. Fluoreszierende Substanz gemäß Anspruch 4, dadurch gekennzeichnet, daß die fluoreszierende Substanz Nd und Yb enthält, wobei das Stoffmengenverhältnis von Nd zu Yb (Nd:Yb) im Bereich von 9:1 bis 5:5 liegt.
8. Fluoreszierende Substanz gemäß irgendeinem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Anstiegszeit, die notwendig ist, damit die Intensität der fluoreszierenden Substanz nach der Bestrahlung mit dem anregenden Licht 90 % der maximalen Intensität erreicht, innerhalb von 200 µs liegt.
9. Fluoreszierende Substanz gemäß irgendeinem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Abfallzeit, die notwendig ist, damit die Intensität des fluoreszierenden Lichts nach der Unterbrechung der Bestrahlung um 80 % der maximalen Intensität abgeschwächt wird, innerhalb von 200 µs liegt.
10. Fluoreszierende Zusammensetzung, dadurch gekennzeichnet, daß sie umfaßt eine fluoreszierende Substanz in Form von Ultramikroteilchen, welche befähigt sind, fluoreszierendes Licht einer Wellenlänge zu emittieren, die von derjenigen eines anregenden Lichts verschieden ist, und die eine durchschnittliche Teilchengröße haben, die kleiner als die Wellenlänge der maximalen Intensität des fluoreszierenden Lichts ist, ein Bindemittel, das sowohl gegenüber dem anregenden Licht als auch dem fluoreszierenden Licht durchlässig ist, und ein Lösungsmittel.
11. Fluoreszierende Zusammensetzung, dadurch gekennzeichnet, daß sie umfaßt: eine fluoreszierende Substanz in Form von Ultramikroteilchen, welche befähigt sind, fluoreszierendes Licht einer Wellenlänge zu emittieren, die von derjenigen eines anregenden Lichts verschieden ist, und die eine durchschnittliche Teilchengröße haben, die kleiner als die Wellenlänge der maximalen Intensität des anregenden Lichts ist, ein Bindemittel, das sowohl gegenüber dem anregenden Licht als auch dem fluoreszierenden Licht durchlässig ist, und ein Lösungsmittel.
12. Fluoreszierende Zusammensetzung gemäß den Ansprüchen 10 oder 11, dadurch gekennzeichnet, daß die fluoreszierende Zusammensetzung als Abtönmedium für einen Tintenstrahldrucker verwendet wird.
13. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 12, dadurch gekennzeichnet, daß die fluoreszierende Substanz eine metallorganische Verbindung umfaßt.
14. Fluoreszierende Zusammensetzung gemäß Anspruch 13, dadurch gekennzeichnet, daß das organische Material,

das in der metallorganischen Verbindung enthalten ist, wenigstens ein Element ist, das aus der aus Carbonsäure, Keton, Ether und Amin bestehenden Gruppe ausgewählt ist.

- 5 15. Fluoreszierende Zusammensetzung gemäß Anspruch 13, dadurch gekennzeichnet, daß die metallorganische Verbindung wenigstens ein organisches Material ist, das aus der aus Neodymcinnamat, Komplexsalz aus Zimtsäure mit Neodym und Ytterbium, Komplexsalz aus Benzoesäure mit Neodym und Ytterbium, Neodymnaphthoat und Komplexsalz aus Naphthoesäure mit Neodym und Ytterbium bestehenden Gruppe ausgewählt ist.
- 10 16. Fluoreszierende Zusammensetzung gemäß Anspruch 13, dadurch gekennzeichnet, daß die fluoreszierende Substanz Nd und Yb enthält, wobei das Stoffmengenverhältnis von Nd zu Yb (Nd:Yb) im Bereich von 9:1 bis 5:5 liegt.
17. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß die Dichte  $p_1$  der fluoreszierenden Substanz und die Dichte  $p_2$  des Bindemittels eine Beziehung von  $p_1/p_2 \leq 1,8$  haben.
- 15 18. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß die fluoreszierende Zusammensetzung eine Viskosität im Bereich von 2 bis 25 cp-s hat.
19. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß die fluoreszierende Zusammensetzung eine Oberflächenspannung im Bereich von 23 bis 40 dyn/cm hat.
- 20 20. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß die fluoreszierende Zusammensetzung einen spezifischen Widerstand hat, der nicht größer als 2000  $\Omega$ -cm ist.
- 25 21. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß die fluoreszierende Zusammensetzung einen pH im Bereich von 4,5 bis 10 hat.
22. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß das Bindemittel ein wasserlösliches Harz ist.
- 30 23. Fluoreszierende Zusammensetzung gemäß Anspruch 22, dadurch gekennzeichnet, daß das Lösungsmittel Wasser und eine leicht zu verflüchtigende Flüssigkeit ist, die mit Wasser kompatibel ist.
- 35 24. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß das Bindemittel eine Lichtdurchlässigkeit von nicht weniger als 80 % in bezug auf sowohl das anregende Licht als auch das fluoreszierende Licht hat.
- 40 25. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß das Bindemittel ein in Wasser nichtlösliches Harz ist.
- 45 26. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß die fluoreszierende Substanz von einer Art ist, die eine Anstiegszeit hat, welche erforderlich ist, damit die Intensität des fluoreszierenden Lichts nach dem Beginn der Bestrahlung mit anregendem Licht 90 % der maximalen Intensität erreicht, die innerhalb von 200  $\mu$ s liegt.
- 50 27. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß die fluoreszierende Substanz von einer Art ist, die eine Abfallzeit hat, welche erforderlich ist, damit die Intensität des fluoreszierenden Lichts nach der Unterbrechung der Bestrahlung auf 80 % der maximalen Intensität abgeschwächt wird, die innerhalb von 200  $\mu$ s liegt.
- 55 28. Fluoreszierende Zusammensetzung gemäß irgendeinem der Ansprüche 10 bis 16, dadurch gekennzeichnet, daß ein Farbstoff zugefügt wird.
29. Fluoreszierender Markierungsträger, dadurch gekennzeichnet, daß er eine darauf gebildete fluoreszierende Tintenabscheidung aufweist, wobei die fluoreszierende Tintenabscheidung, die eine fluoreszierende Substanz enthält, welche befähigt ist, fluoreszierendes Licht einer Wellenlänge zu emittieren, die von der des anregenden Lichts verschieden ist, und die eine durchschnittliche Teilchengröße aufweist, die kleiner als die Wellenlänge der maximalen Intensität des fluoreszierenden Lichts ist, darauf gedruckt ist.

30. Fluoreszierender Markierungsträger, dadurch gekennzeichnet, daß er eine darauf gebildete fluoreszierende Tintenabscheidung aufweist, wobei die fluoreszierende Tintenabscheidung, die eine fluoreszierende Substanz enthält, welche befähigt ist, fluoreszierendes Licht einer Wellenlänge zu emittieren, die von der des anregenden Lichts verschieden ist, und die eine durchschnittliche Teilchengröße aufweist, die kleiner als die Wellenlänge der maximalen Intensität des anregenden Lichts ist, darauf gedruckt ist.
31. Fluoreszierender Markierungsträger gemäß den Ansprüchen 29 oder 30, dadurch gekennzeichnet, daß die fluoreszierende Tintenabscheidung durch einen Tintenstrahldrucker gebildet wird.
32. Fluoreszierender Markierungsträger gemäß irgendeinem der Ansprüche 29 bis 31, dadurch gekennzeichnet, daß die fluoreszierende Substanz eine metallorganische Verbindung umfaßt.
33. Fluoreszierender Markierungsträger gemäß Anspruch 32, dadurch gekennzeichnet, daß ein organisches Material, das in der metallorganischen Verbindung enthalten ist, wenigstens ein Element ist, das aus der aus Carbonsäure, Keton, Ether und Amin bestehenden Gruppe ausgewählt ist.
34. Fluoreszierender Markierungsträger gemäß Anspruch 33, dadurch gekennzeichnet, daß die metallorganische Verbindung wenigstens ein organisches Material ist, das aus der aus Neodymcinnamat, Komplexsalz aus Zimtsäure mit Neodym und Ytterbium, Komplexsalz aus Benzoesäure mit Neodym und Ytterbium, Neodymnaphthoat und Komplexsalz aus Naphthoesäure mit Neodym und Ytterbium bestehenden Gruppe ausgewählt ist.
35. Fluoreszierender Markierungsträger gemäß Anspruch 32, dadurch gekennzeichnet, daß die fluoreszierende Substanz Nd und Yb enthält, wobei das Stoffmengenverhältnis von Nd zu Yb (Nd:Yb) im Bereich von 9:1 bis 5:5 liegt.
36. Fluoreszierender Markierungsträger gemäß den Ansprüchen 29 oder 30, dadurch gekennzeichnet, daß die fluoreszierende Tintenabscheidung ein Bindemittel in einer Menge von nicht weniger als 5 Gew.-% enthält.

## Revendications

1. Substance fluorescente d'un type capable d'émettre, en réponse à une irradiation de lumière d'excitation, une lumière fluorescente d'une longueur d'onde différente de celle de la lumière d'excitation, caractérisée en ce que la granulométrie moyenne de la substance fluorescente est inférieure à la longueur d'onde de la lumière fluorescente à l'intensité maximale de cette lumière fluorescente émise par cette substance fluorescente.
2. Substance fluorescente d'un type capable d'émettre, en réponse à une irradiation de lumière d'excitation, une lumière fluorescente d'une longueur d'onde différente de celle de la lumière d'excitation, caractérisée en ce que la granulométrie moyenne de la substance fluorescente est inférieure à la longueur d'onde de la lumière fluorescente à l'intensité maximale de la lumière d'excitation.
3. Substance fluorescente selon la revendication 1 ou 2, caractérisée en ce que la granulométrie moyenne de la substance fluorescente n'est pas supérieure à 0,8 µm.
4. Substance fluorescente selon l'une quelconque des revendications 1 à 3, caractérisée en ce que la substance fluorescente est un composé métallique organique contenant au moins du Nd à titre d'élément actif optique.
5. Substance fluorescente selon la revendication 4, caractérisée en ce que le composé métallique organique contient au moins un matériau organique choisi dans le groupe constitué par un acide carboxylique, une cétone, un éther et une amine.
6. Substance fluorescente selon la revendication 4, caractérisée en ce que le composé métallique organique est au moins un matériau organique choisi dans le groupe constitué par le cinnamate de néodyme, un sel complexe d'acide cinnamique avec du néodyme et de l'ytterbium, un sel complexe d'acide benzoïque avec du néodyme et de l'ytterbium, le naphthoate de néodyme, et un sel complexe d'acide naphthoïque avec du néodyme et de l'ytterbium.
7. Substance fluorescente selon la revendication 4, caractérisée en ce que la substance fluorescente contient du Nd et du Yb, le rapport molaire du Nd par rapport au Yb (Nd/Yb) étant situé dans la plage allant de 9/1 à 5/5.



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8. Substance fluorescente selon l'une quelconque des revendications 1 à 7, caractérisée en ce que le temps de montée requis pour que l'intensité de la substance fluorescente atteigne 90 % de son intensité maximale après irradiation de la lumière d'excitation est de l'ordre de 200  $\mu$ s.
- 5 9. Substance fluorescente selon l'une quelconque des revendications 1 à 8, caractérisée en ce que le temps de descente requis pour que l'intensité de la lumière fluorescente s'atténue de 80 % de son intensité maximale après interruption de l'irradiation est de l'ordre de 200  $\mu$ s.
- 10 10. Composition fluorescente, caractérisée en ce qu'elle comprend une substance fluorescente sous la forme d'ultra-microparticules, capable d'émettre une lumière fluorescente ayant une longueur d'onde différente de celle d'une lumière d'excitation et ayant une granulométrie moyenne inférieure à la longueur d'onde de l'intensité maximale de la lumière fluorescente, un liant transparent tant pour la lumière d'excitation que pour la lumière fluorescente, et un solvant.
- 15 11. Composition fluorescente, caractérisée en ce qu'elle comprend une substance fluorescente sous la forme d'ultra-microparticules, capable d'émettre une lumière fluorescente ayant une longueur d'onde différente de celle d'une lumière d'excitation et ayant une granulométrie moyenne inférieure à la longueur d'onde de l'intensité maximale de la lumière d'excitation, un liant transparent tant pour la lumière d'excitation que pour la lumière fluorescente, et un solvant.
- 20 12. Composition fluorescente selon la revendication 10 ou 11, caractérisée en ce que la composition fluorescente est utilisée en tant que milieu d'encrage pour une imprimante à jet d'encre.
- 25 13. Composition fluorescente selon l'une quelconque des revendications 10 à 12, caractérisée en ce que la substance fluorescente est constituée d'un composé métallique organique.
- 30 14. Composition fluorescente selon la revendication 13, caractérisée en ce qu'un matériau organique contenu dans le composé métallique est au moins un élément choisi dans le groupe constitué par un acide carboxylique, une cétone, un éther et une amine.
- 35 15. Composition fluorescente selon la revendication 13, caractérisée en ce que le composé métallique organique est au moins un matériau organique choisi dans le groupe constitué par le cinnamate de néodyme, un sel complexe d'acide cinnamique avec du néodyme et de l'ytterbium, un sel complexe d'acide benzoïque avec du néodyme et de l'ytterbium, le naphthoate de néodyme, et un sel complexe d'acide naphthoïque avec du néodyme et de l'ytterbium.
- 40 16. Composition fluorescente selon la revendication 3, caractérisée en ce que la substance fluorescente contient du Nd et du Yb, le rapport molaire du Nd par rapport au Yb (Nd/Yb) étant situé dans la plage allant de 9/1 à 5/5.
17. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que la densité  $p_1$  de la substance fluorescente et la densité  $p_2$  du liant ont la relation  $p_1/p_2 \leq 1,8$ .
18. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que la composition fluorescente a une viscosité située dans la plage allant de 2 à 25 cP.
- 45 19. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que la composition fluorescente a une tension superficielle située dans la plage allant de 23 à 40 dynes/cm.
20. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que la composition fluorescente a une résistance spécifique non supérieure à 2000  $\Omega$ cm.
- 50 21. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que la composition fluorescente a une valeur de pH située dans la plage allant de 4,5 à 10.
- 55 22. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que le liant est une résine soluble dans l'eau.
23. Composition fluorescente selon la revendication 22, caractérisée en ce que le solvant est de l'eau et un liquide facilement volatilisable compatible avec l'eau.

24. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que le liant a un facteur de transmission de la lumière non inférieur à 80 % en ce qui concerne tant la lumière d'excitation que la lumière fluorescente.
- 5 25. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que le liant est une résine insoluble dans l'eau.
26. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que la substance fluorescente est d'un type ayant un temps de montée, requis pour que l'intensité de la lumière fluorescente atteigne 90 % de son intensité maximale après le début de l'irradiation de la lumière d'excitation, qui est de l'ordre de 200  $\mu$ s.
- 10 27. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce que la substance fluorescente est d'un type ayant un temps de descente requis pour que l'intensité de la lumière fluorescente s'atténue de 80 % de son intensité maximale après interruption de l'irradiation, qui est de l'ordre de 200  $\mu$ s.
- 15 28. Composition fluorescente selon l'une quelconque des revendications 10 à 16, caractérisée en ce qu'une charge colorante est ajoutée.
- 20 29. Support de signe fluorescent, caractérisé en ce qu'il a un dépôt d'encre fluorescente formé dessus, ledit dépôt d'encre fluorescente, contenant une substance fluorescente capable d'émettre une lumière fluorescente ayant une longueur d'onde différente de celle de la lumière d'excitation et ayant une granulométrie moyenne inférieure à la longueur d'onde de l'intensité maximale de la lumière fluorescente, étant imprimé dessus.
- 25 30. Support de signe fluorescent, caractérisé en ce qu'il a un dépôt d'encre fluorescente formé dessus, ledit dépôt d'encre fluorescente, contenant une substance fluorescente capable d'émettre une lumière fluorescente ayant une longueur d'onde différente de celle de la lumière d'excitation et ayant une granulométrie moyenne inférieure à la longueur d'onde de l'intensité maximale de la lumière d'excitation, étant imprimé dessus.
- 30 31. Support de signe fluorescent selon la revendication 29 ou 30, caractérisé en ce que le dépôt d'encre fluorescente est formé par une imprimante à jet d'encre.
32. Support de signe fluorescent selon l'une quelconque des revendications 29 à 31, caractérisé en ce que la substance fluorescente est constituée d'un composé métallique organique.
- 35 33. Support de signe fluorescent selon la revendication 32, caractérisé en ce qu'un matériau organique contenu dans le composé métallique organique est au moins un élément choisi dans le groupe constitué par un acide carboxylique, une cétone, un éther et une amine.
- 40 34. Support de signe fluorescent selon la revendication 33, caractérisé en ce que le composé métallique organique est au moins un matériau organique choisi dans le groupe constitué par le cinnamate de néodyme, un sel complexe d'acide cinnamique avec du néodyme et de l'ytterbium, un sel complexe d'acide benzoïque avec du néodyme et de l'ytterbium, le naphthoate de néodyme, et un sel complexe d'acide naphthoïque avec du néodyme et de l'ytterbium.
- 45 35. Support de signe fluorescent selon la revendication 32, caractérisé en ce que la substance fluorescente contient du Nd et du Yb, le rapport molaire du Nd par rapport au Yb (Nd/Yb) étant situé dans la plage allant de 9/1 à 5/5.
- 50 36. Support de signe fluorescent selon la revendication 29 ou 30, caractérisé en ce que le dépôt d'encre fluorescente contient un liant en une quantité non inférieure à 5 % en poids.

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Fig.1

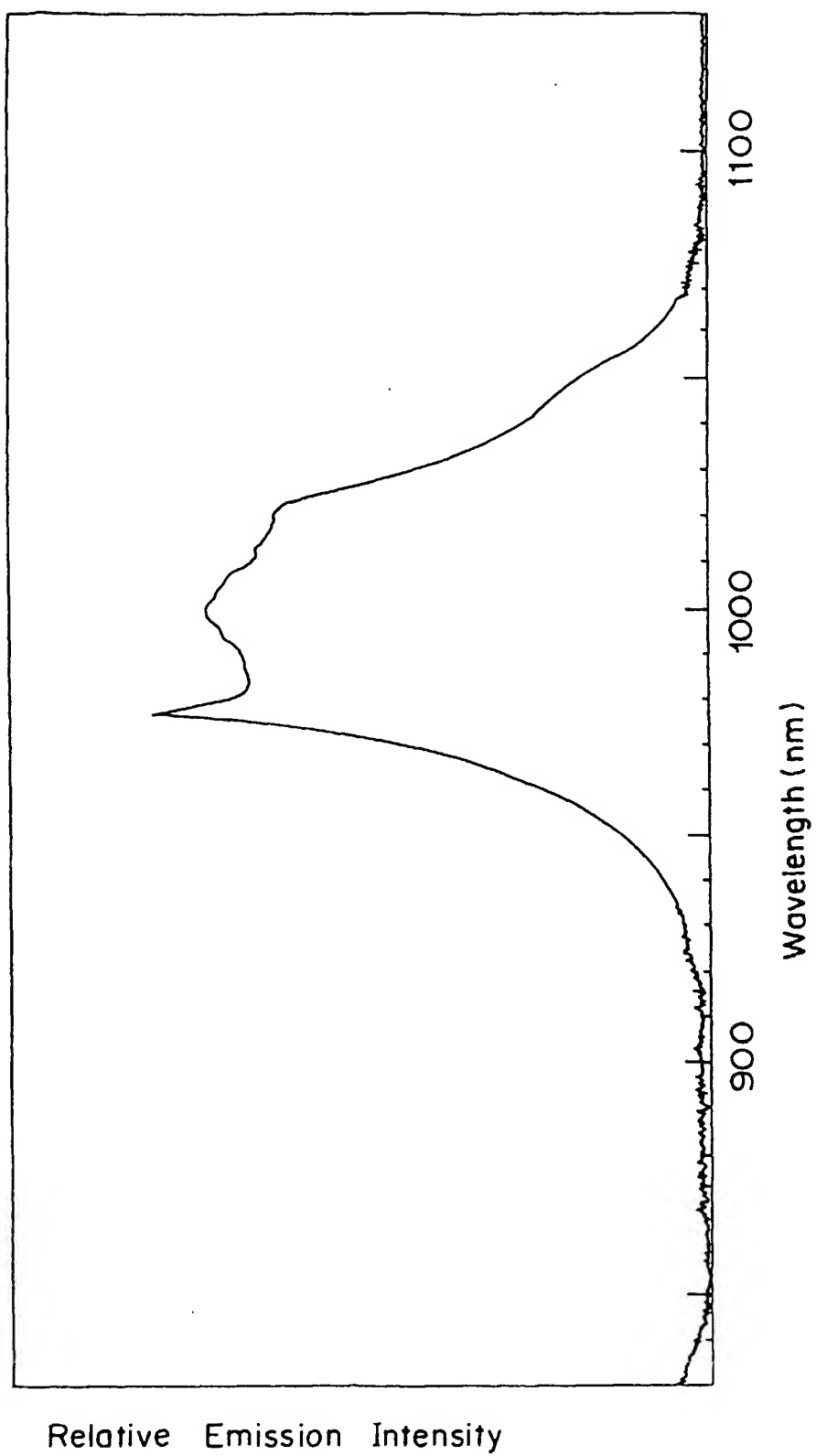


Fig.3A

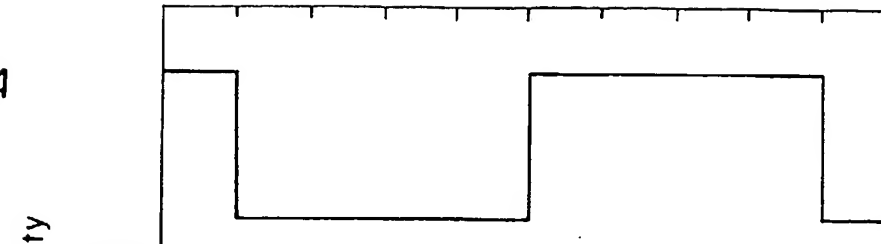


Fig.3B

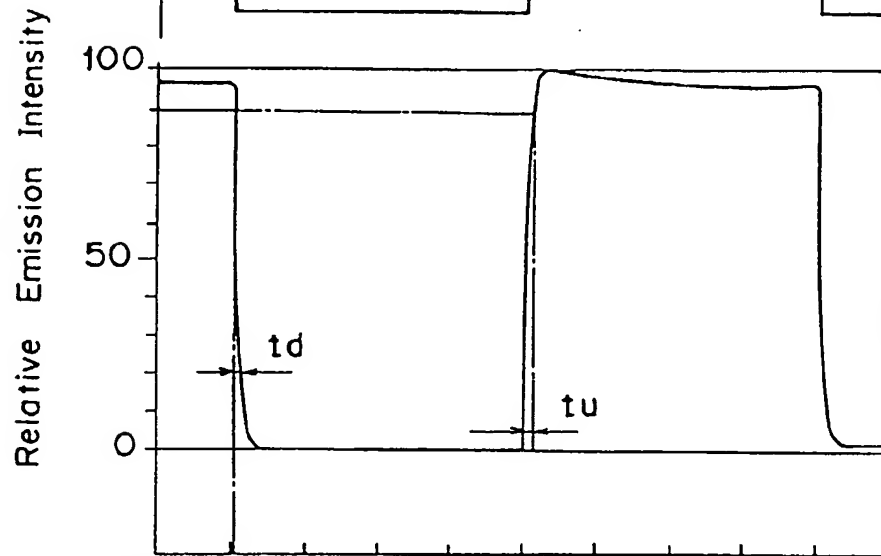


Fig.3C

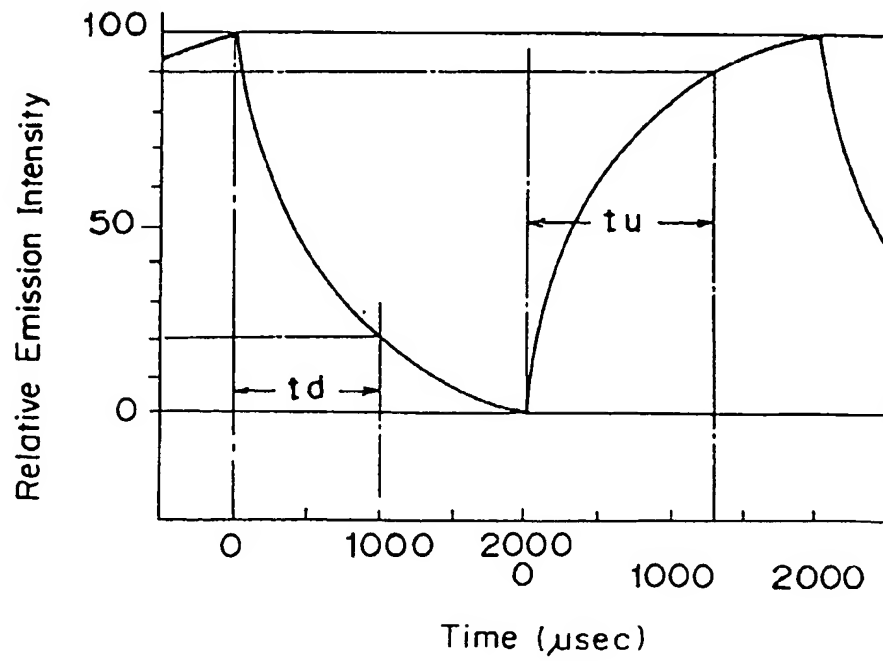


Fig. 2

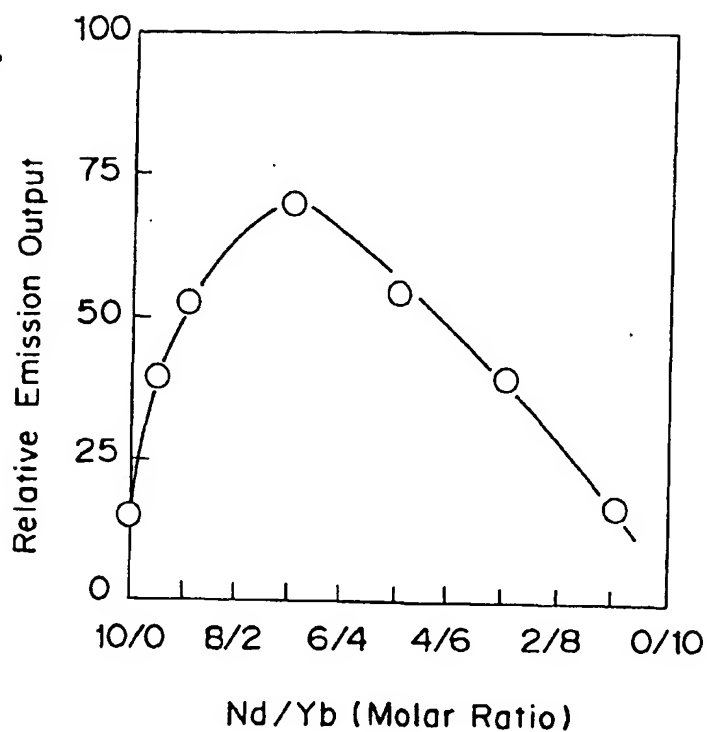


Fig. 4

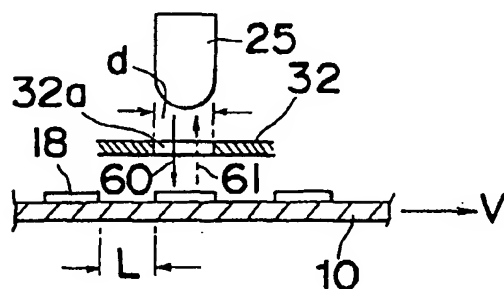
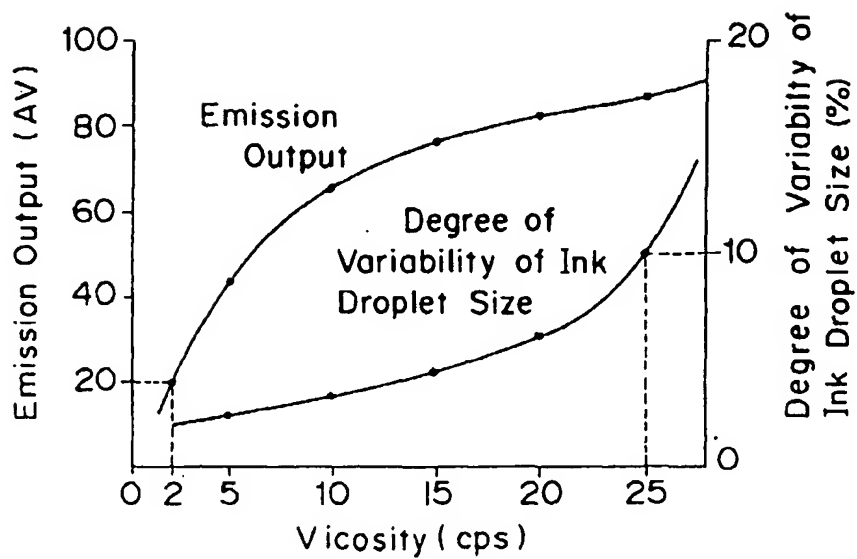


Fig. 5



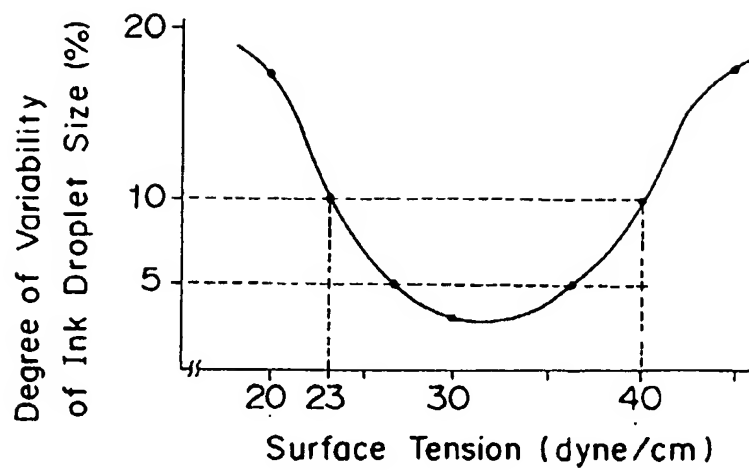
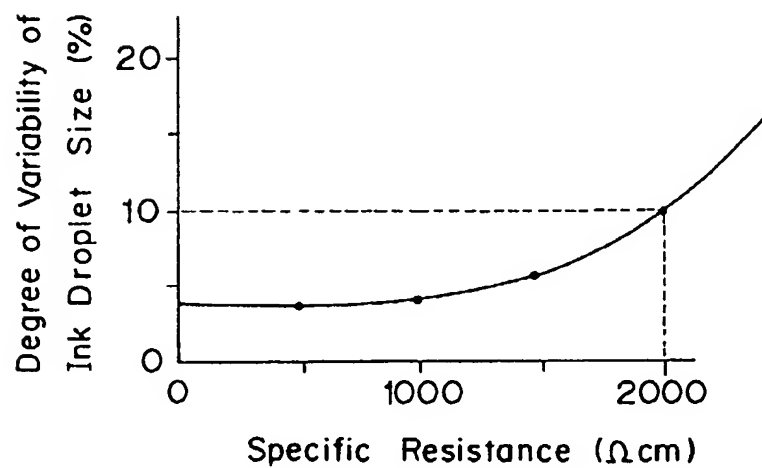
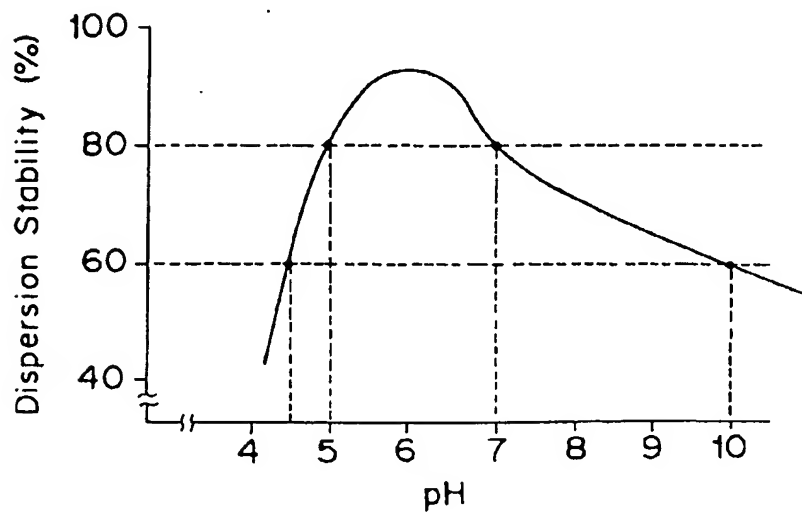
*Fig. 6**Fig. 7**Fig. 8*

Fig. 9

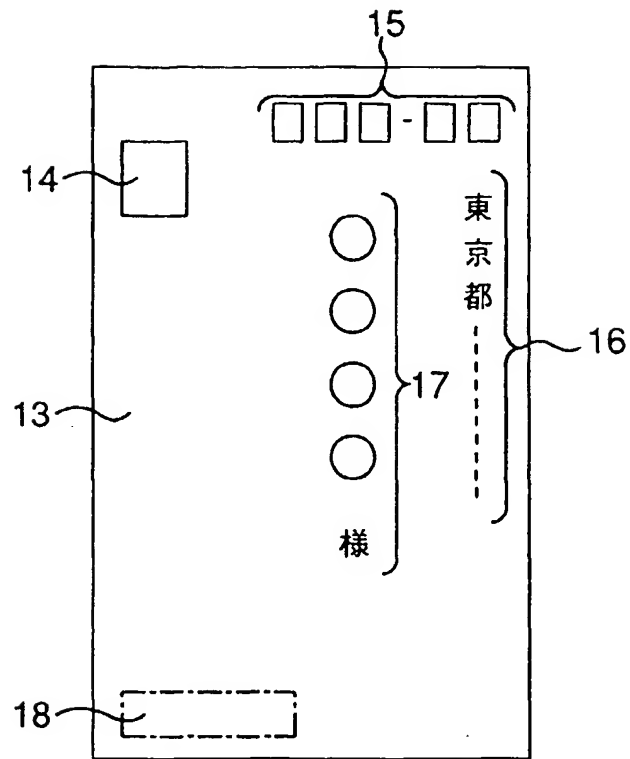


Fig. 10

